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CXIX.—ON NITROMALONIC ALDEHYDE.

[SECOND PAPER.]

BY HENRY B. HILL.

ON THE CONDENSATION OF NITROMALONIC ALDEHYDE WITH CERTAIN KETONES AND KETONE-ACIDS.

BY CHARLES A. SOCH AND GEORGE OENSLAGER.

In a former paper[1] it was shown that nitromalonic aldehyde readily entered into reaction with acetone in alkaline solution, and that the product formed was *p*-nitrophenol. Certain results which had already been obtained by Messrs. Soch and Oenslager were also mentioned, which showed that the reaction could easily be extended to other ketones and to ketone-acids. Although their investigation was at that time essentially completed, a few experimental details still needed revision, and as both of these gentlemen had already left Cambridge, the publication of their results has necessarily been delayed.

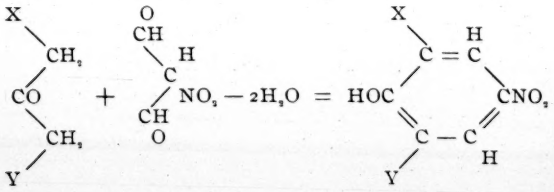
In order to establish the general nature of the reaction it seemed advisable to select for study a few typical ketones and ketone-acids, but to make no attempt to extend the investigation in such way as to cover a large number of bodies

[1] This JOURNAL, **22**, 89.

which might easily be prepared. Methylethyl ketone and dibenzyl ketone were accordingly selected as typical ketones, while acetacetic ester, levulinic acid and acetone dicarboxylic acid were chosen to represent the ketone-acids. Certain other bodies of similar nature, which promise to yield condensation products of peculiar interest, may be studied in the future.

It was found that condensation took place most neatly in dilute (normal) aqueous solution with the addition of a slight excess of sodic hydrate. With acetacetic ester two molecules of sodic hydrate were needed, and saponification of the ester doubtless preceded the condensation, but in other cases a feebly alkaline solution only was required; at the same time an excess of one molecule did no harm and somewhat shortened the time needed to complete the reaction. In the case of the dibenzyl ketone the reaction ran so slowly in aqueous solution that dilute alcohol was taken as the solvent. In each case the condensation seemed to take place most smoothly in the cold; while heat naturally hastened the reaction, the product was then dark colored and the yield diminished. At ordinary temperatures the decomposition was essentially completed in the course of twenty-four or at most forty-eight hours, and so large a product was obtained in each case that the reaction might fairly be called quantitative.

The structure of the bodies prepared from nitromalonic aldehyde by condensation was so well established by the mode of their formation,



that no especial effort was made to obtain confirmatory evidence as to their constitution. At the same time a certain amount of such evidence was collected in the course of the work. From methylethyl ketone a nitrocresol was obtained

which melted at 94–95° and which was apparently identical with the (*a*) *m*-nitroorthocresol of Nevile and Winther[1] melting at this point. It gave, on reduction, an amidocresol which melted at 172°–173° (uncorr.) and this in turn gave toluquinone on oxidation. According to Nölting and Kohn[2] the (*a*) *m*-amidoorthocresol melts at 172°–173° The nitrosalicylic which was obtained from acetacetic ester melted at 228° and was therefore the (*a*) *m*-nitrosalicylic acid the structure of which was established by Hübner.[3] The dibasic acid formed from acetone dicarboxylic acid must have its carboxyls adjacent to the hydroxyl with the nitro group in the para place. Through the action of fuming nitric acid it was converted, as is also the (*a*) *m*-nitrosalicyilic acid, into picric acid (2, 4, 6-trinitrophenol.)

The diphenylnitrophenol formed from dibenzyl ketone could be converted into the corresponding quinone by successive reduction and oxidation; the para relation of the nitro and the hydroxyl groups was thus established but no additional evidence as to the position of the phenyl groups was obtained.

Quite recently Borsche[4] has published an interesting account of his work upon the action of diazobenzol chloride upon an alkaline solution of nitrosophenol. He describes two bodies, which he calls nitrosooxydiphenyl and nitrosooxydiphenyl benzol. While he was unable at the time to prove the structure of the bodies in question, he very properly assumes that they are probably formed by the introduction of the phenyl group in the ortho position to the hydroxyl. He did not succeed in preparing the corresponding nitrophenols by oxidation, but by reduction he obtained the related amidophenols and from them the quinones and the hydroquinones. His description of the latter bodies agrees well with the observations of Soch and Oenslager, although the melting-points which he gives do not agree sharply with their determinations.

1 Ber. d. chem. Ges., **15**, 2978.
2 *Ibid.*, **17**, 365.
3 Ann. Chem. (Liebig), **195**, 1.
4 Ber. d. chem. Ges., **32**, 2935.

	Borsche.	S. & O. (corr.)
Amidophenol	146°–147°	149°–150°
Quinone	137°–138°	135°–136°
Hydroquinone	177°–178°	179°–180°

In spite of the discrepancies between these two sets of figures, the general agreement is such that one cannot doubt the identity in structure of the two series.

Borsche's paper was unfortunately overlooked at the time of its publication, and in the meantime Mr. W. J. Hale had already prepared from methylbenzyl ketone the *o*-phenyl-*p*-nitrophenol together with the corresponding amidophenol and quinone. These derivatives of diphenyl, which were of interest in that both substituting groups were in the same benzol ring, agree well with the brief description of the similar compounds made from nitrosooxydiphenyl given by Borsche, but his melting-points are in both cases several degrees lower.

Methylethyl Ketone.

(*a*) *m-Nitroorthocresol*, $C_7H_7NO_3$.—To a saturated aqueous solution of sodium nitromalonic aldehyde rather more than one molecule of methylethyl ketone was added, and the solution was then made alkaline by the addition of sodic hydrate. An orange-yellow color was rapidly developed, but, if the amount of sodic hydrate added was small (0.2 molecule), no precipitate was formed. After standing in the cold for 24 hours the reaction was apparently at an end and hydrochloric acid then threw down an oil, which gradually solidified as the excess of the ketone evaporated. The weight of the crude product thus obtained was 88 per cent of the theoretical amount of the nitrocresol which should be formed from the sodium nitromalonic aldehyde taken. It melted at 90°–91°, but this melting-point could easily be raised by recrystallization from ligroin, or from a mixture of ether and ligroin, until it reached 94°–95° (uncorr.). Analysis then showed that the body had the composition of a nitrocresol.

0.1363 gram substance dried *in vacuo* over sulphuric acid gave 0.2710 gram CO_2 and 0.0620 gram H_2O.

	Calculated for $C_7H_7NO_3$	Found.
C	54.88	54.24
H	4.61	5.09

This nitrocresol was readily soluble in alcohol, ether, chloroform or benzol, but more sparingly soluble in ligroin. Its sodium salt was readily soluble in water, but separated from its aqueous solution on the addition of sodic hydrate in slender orange-yellow needles. Its melting-point, 94°–95° (uncorr.), corresponds exactly with that given by Nevile and Winther[1] 94°.6–95°, for their (*a*) *m*-nitroorthocresol. In order to prove the identity a little more rigorously it was reduced with tin and hydrochloric acid, and the amidocresol precipitated from the solution of the hydrochloride, after the removal of the tin, by the addition of sodic carbonate. The melting-point of the substance purified by recrystallization from benzol proved to be 172°–173° (uncorr.) in precise agreement with the point given by Nölting and Kohn[2] for (*a*) *m*-amidoorthocresol purified in the same way. On oxidation with sulphuric acid and potassic dichromate in the usual way it gave toluquinone melting at 67°–68° (corr.).

Dibenzyl Ketone.

2,6-Diphenyl-4-nitrophenol, $C_{18}H_{13}NO_3$—Dibenzyl ketone reacts with sodium nitromalonic aldehyde in slightly alkaline aqueous solution, but the ketone is so slightly soluble in water that the progress of the reaction is extremely slow. Even with dilute alcohol as a solvent the reaction runs slowly, if but a small amount (0.25 molecule) of sodic hydrate is used. It is, therefore, more convenient to dissolve the ketone in four times its weight of alcohol, to add 2 molecules of sodic hydrate in normal solution and then the equivalent amount of sodium nitromalonic aldehyde. A great part of the dibenzyl ketone is precipitated by the dilution of its alcoholic solution with the aqueous sodic hydrate, but, if the whole is constantly shaken, it gradually goes into solution, and at the end of a few hours it has disappeared. The deep orange-red solution is allowed to stand over night in order

[1] Ber. d. chem. Ges., **15**, 2978.
[2] *Ibid.*, **17**, 365.

to complete the reaction, and the alcohol then driven off upon the water-bath. Even after the addition of water to restore the original volume of the solution a large amount of a deep red sodium salt separates. Hydrochloric acid throws down a viscous mass, which gradually hardens, and may then be recrystallized from alcohol. If, however, carbonic dioxide is passed into the solution the crystalline sodium salt gradually disappears as the excess of sodic hydrate is neutralized and crystals of the new nitrophenol begin to take their place. As soon as the liquid is saturated with carbonic dioxide the heavy crystalline precipitate is collected upon a filter and washed with cold water until the wash-water is no longer colored. In this way 94.5 per cent of the theoretical yield of the phenol may be obtained, and in such a pure condition that recrystallization fails to raise its melting-point materially.

0.1577 gram substance dried at 100° gave 0.4282 gram CO_2 and 0.0703 gram H_2O.

	Calculated for $C_{18}H_{13}NO_3$.	Found.
C	74.20	74.06
H	4.50	4.99

The 2,6-diphenyl-4-nitrophenol is readily soluble in ether, chloroform, or benzol, but is sparingly soluble in ligroin. It dissolves freely in boiling alcohol, but as the solution cools the greater part separates in flat, obliquely truncated prisms, which usually collect together in the form of leafy aggregations. It melts at 135°–136° (corr.).

Potassic 2,6-diphenyl-4-nitrophenylate, $C_{18}H_{12}NO_3K.H_2O$.—The potassium salt is sparingly soluble in cold water, more readily soluble in hot water, and dissolves readily in alcohol; it may conveniently be recrystallized from dilute alcohol. It forms short yellow needles, which contain one molecule of water of crystallization. They lose this molecule of water slowly over sulphuric acid, more rapidly at 100°, and at the same time change their color to a brilliant red.

0.4589 gram salt lost at 100° 0.0264 gram H_2O.

	Calculated for $C_{18}H_{12}NO_3K.H_2O$.	Found.
H_2O	5.19	5.75

I. 0.2041 gram anhydrous salt gave 0.0525 gram K_2SO_4.
II. 0.2058 gram anhydrous salt gave 0.0544 gram K_2SO_4.

	Calculated for $C_{18}H_{12}NO_3K$.	Found. I.	II.
K	11.89	11.55	11.87

2,6-Diphenyl-4-nitroanisol, $C_{19}H_{15}NO_3$.—This body was made in the usual way by the action of methyl iodide upon the potassium salt. It is readily soluble in chloroform, benzol or carbonic disulphide, more sparingly soluble in ether and very sparingly soluble in boiling alcohol or ligroin. It may most readily be crystallized from alcohol with the addition of a little chloroform, and forms clear, clustered, oblique prisms which melt at 152°–153° (corr.).

0.1433 gram substance gave 0.3900 gram CO_2 and 0.0636 gram H_2O.

	Calculated for $C_{19}H_{15}NO_3$.	Found.
C	74.71	74.25
H	4.95	4.97

2,6-Diphenyl-4-amidophenol, $C_{18}H_{15}NO$.—The nitrophenol is readily reduced by tin and hydrochloric acid, if a little alcohol is at the same time added. The hydrochlorate of the base which is formed is sparingly soluble in cold water, more readily soluble in hot water, but its solubility even in hot water is greatly diminished by the addition of a small percentage of hydrochloric acid. The free base was separated in the usual way by the addition of potassic carbonate, and purified by recrystallization from benzol.

0.1509 gram substance gave 7.8 cc. moist nitrogen at 28° and under a presssure of 743 mm.

	Calculated for. $C_{18}H_{15}NO$.	Found.
N	5.38	5.52

The 2,6-diphenyl-4-amidophenol is readily soluble in alcohol, rather more sparingly soluble in ether, and sparingly soluble even in boiling ligroin. It dissolves readily in hot benzol, and crystallizes as the solution cools in rhombic plates, or commonly in more extended flat, obliquely terminated prisms. When recrystallized from benzol it shows the constant melting-point 149°–150° (corr.). The pure base is

unchanged by tolerably long exposure to the air, but the impure body rapidly turns red.

a-Diphenylbenzoquinone, $C_{18}H_{12}O_2$.—The diphenylamidophenol was oxidized with potassic dichromate and sulphuric acid diluted with three times its weight of water. The sulphate of the base proved to be very sparingly soluble in the dilute sulphuric acid, and no oxidation was noticed at ordinary temperatures even after long standing. On warming on the water-bath a slow reaction set in, which was apparently completed after several hours heating. The red crystalline product was then collected upon a filter and well washed with water. The quinone may be purified by recrystallization from 80 per cent acetic acid, or by dissolving it in chloroform, evaporating the filtered solution and recrystallizing the red crystalline residue from alcohol.

I. 0.1494 gram substance gave 0.4518 gram CO_2 and 0.0657 gram H_2O.

II. 0.1400 gram substance gave 0.4232 gram CO_2 and 0.0605 gram H_2O.

	Calculated for $(C_{18}H_{12}O)_2$.	Found. I.	II.
C	83.07	82.49	82.45
H	4.66	4.92	4.83

The 2,6-diphenylbenzoquinone is very readily soluble in chloroform, quite readily soluble in benzol or carbonic disulphide, more sparingly soluble in ether and very sparingly soluble in ligroin. It dissolves with difficulty in boiling alcohol, and crystallizes as the solution cools in long slender needles. Hot glacial acetic acid dissolves it freely and deposits it on cooling, but an 80 per cent acetic acid is a more convenient solvent. When recrystallized from alcohol or from acetic acid it melts at 135°–136° (corr.), and by sublimation it may be obtained in felted, orange-red needles which melt at the same point. When exposed to direct sunlight the red color soon fades and the melting-point is at the same time materially lowered; this change has not been further studied. With concentrated sulphuric acid it gives a blue green coloration.

(*a*) *Diphenylhydroquinone*, $C_{18}H_{14}O_2$.—Sulphurous dioxide

can not advantageously be used for the reduction of the quinone, on account of its slight solubility in water. With glacial acetic acid and zinc a colorless solution is readily obtained, and the hydroquinone may then be precipitated from the filtered solution by the addition of water.

0.1359 gram substance gave 0.4096 gram CO_2 and 0.0683 gram H_2O.

	Calculated for $C_{18}H_{14}O_2$.	Found.
C	82.43	82.21
H	5.39	5.62

(*a*)-Diphenylhydroquinone is readily soluble in alcohol or ether, sparingly soluble in hot chloroform or benzol and almost insoluble in water, ligroin, or carbonic disulphide. After several recrystallizations from alcohol it formed clear, clustered, oblique prisms which melted at 179°–180° (corr.); further crystallization from chloroform, from which it separated in transparent, rectangular plates, failed to raise this melting-point. In alkaline solution it is rapidly oxidized by exposure to the air with the formation of red needles, which are apparently the quinone, but on further oxidation the latter again disappear.

Acetacetic Ester.

(*a*)-*m-Nitrosalicylic Acid*, $C_7H_5NO_5$.—Nitromalonic aldehyde condenses easily with acetacetic ester provided that two molecules of sodic hydrate at least are used; the product is then the sparingly soluble basic sodium salt of nitrosalicylic acid. It has not been found possible to form the ester of the nitrosalicylic acid directly by the use of a small amount of sodic hydrate. Apparently the saponification of the acetacetic ester by the second molecule of sodic hydrate[1] precedes the condensation. If acetacetic ester is dissolved in a normal solution of two molecules of sodic hydrate and one molecule of sodium nitromalonic aldehyde is added, the color of the solution soon shows that reaction is taking place, and after the lapse of twenty-four hours the solution has nearly solidified with the separation of the long finely-felted, orange needles of the basic sodium salt. The crude acid which

[1] Ber. d. chem. Ges. **32**, 3390.

separates on the addition of hydrochloric acid amounts to 90 per cent of the theoretical weight, and after recrystallization from hot water it has the melting-point, 228°–229° (uncorr.), and the other properties of the long-known (*a*)-*m*-nitrosalicylic acid.

0.1488 gram substance gave 0.2498 gram CO_2 and 0.0420 gram H_2O.

	Calculated for $C_7H_5NO_5$.	Found.
C	45.93	45.78
H	2.75	3.16

On the addition of argentic nitrate to a warm aqueous solution of the free acid the silver salt is at once thrown down. When recrystallized from hot water it forms clustered needles.

0.2698 gram of the salt gave 0.1007 gram silver.

	Calculated for $C_7H_4NO_5Ag$.	Found.
Ag	37.21	37.31

Levulinic Acid.

5-Nitro-2-oxyphenylacetic Acid, $C_8H_7NO_5$.—Pure levulinic acid was dissolved in a slight excess (1.2 molecules) of normal sodic hydrate and a molecule of sodium nitromalonic aldehyde was then added. The color of the solution soon became a deep orange-yellow, and after standing for twenty-four hours hydrochloric acid threw down nitro-oxyphenylacetic acid in well-formed crystals. The slight excess of sodic hydrate somewhat facilitated the reaction, but was not essential. The weight of the product which separated from the dilute solution amounted to 82 per cent of the theoretical yield; by evaporation or extraction of the mother-liquor with ether an additional amount of a somewhat dark colored acid could be obtained. The analysis of substance recrystallized from hot water and dried at 100° gave the following results:

I. 0.1526 gram substance gave 0.2691 gram CO_2 and 0.0530 gram H_2O.

II. 0.1892 gram substance gave 0.3368 gram CO_2 and 0.0685 gram H_2O.

	Calculated for $C_8H_7NO_5$.	Found. I.	Found. II.
C	48.71	48.11	48.54
H	3.58	3.89	4.05

The 5-nitro-2-oxyphenylacetic acid is readily soluble in alcohol or ether, but is sparingly soluble in chloroform, benzol, or ligroin. It dissolves very readily in hot water, more sparingly in cold water, and crystallizes as the solution cools in long slender prisms. On rapid heating the acid melts at 160°–162°, but the melting-point is lowered if the substance is slowly heated. When kept at a temperature of 148°–149° (corr.) it melted in the course of fifteen minutes. This behavior suggested the probable formation of an anhydride, and the *o*-oxyphenylacetic acid has already been shown by v. Baeyer and Fritsch[1] to pass by distillation into its lactone.

Lactone of the 5-Nitro-2-oxyphenylacetic Acid, $C_8H_5NO_4$.—If the nitro-oxyphenylacetic acid is melted by prolonged heating at 148°–149° and the temperature is maintained at this point, it gradually solidifies with the separation of long clear prisms, and is then found to have lost in weight an amount nearly corresponding to one molecule of water.

0.4648 gram acid lost at 148° 0.0408 gram H_2O.

	Calculated for $C_8H_7NO_5$.	Found.
H_2O	9.14	8.78

During the long heating there had been a slight loss by sublimation and at the same time a small percentage of the acid had escaped dehydration. While the acid and the anhydride could easily be separated by recrystallization, and the greater part of the highly colored by-product could be removed by treatment with cold acetone, the substance obtained was still highly colored. By sublimation a perfectly colorless product was obtained, but it was difficult to prepare larger quantities of material at ordinary pressures. A more satisfactory yield was obtained by sublimation of the acid in an atmosphere of carbonic dioxide under pressure of 50–60 mm., and at a temperature of 180°–185°. The acid was then but slightly carbonized, and the lactone sublimed in large, colorless, transparent prisms, or in flat, blade-like forms. The

[1] Ber. d. chem. Ges. **17**, 975.

body was then crystallized from glacial acetic acid, since its melting-point could be slightly raised in this way.

0.2204 gram substance gave 0.4328 gram CO_2 and 0.0682 gram H_2O.

	Calculated for $C_8H_8NO_4$.	Found.
C	53.60	53.57
H	2.81	3.46

This lactone is very sparingly soluble in alcohol, ether, or ligroin, somewhat more readily soluble in chloroform, quite readily soluble in boiling benzol, and still more readily soluble in boiling acetone. It dissolves freely in hot glacial acetic acid, and most of it separates as the solution cools in the form of irregular, pointed needles. On long heating with water it is gradually converted into the acid. It melts at 187°–188° (corr.). This melting-point is so high as compared with that of the acid that it seemed not improbable that a dimolecular anhydride had been formed. A determination of its molecular weight, however, through the boiling-point of its solution in benzol, showed that it was a lactone of ordinary form. 19.6 grams of benzol were employed with the following results:

Substance.	Elevation.	Molecular weight.
0.0914	0.068	183.1
0.1434	0.107	182.5

The calculated molecular weight for the lactone is 179.

5-Nitro-2-oxyphenylacetic Ethyl Ester, $C_{10}H_{11}NO_4$.—This ester is formed even by warming an alcoholic solution of the acid, and may be prepared by heating the acid with a 3 per cent solution of hydrochloric acid in absolute alcohol. It dissolves with a yellow color in sodic carbonate, but is hardly attacked by acid sodic carbonate. It is sparingly soluble in ether, more readily soluble in boiling chloroform or benzol and is nearly insoluble in ligroin. From hot alcohol it crystallizes well in clear, flat, pointed prisms, which frequently expand to form six-sided plates. It melts at 154°–155° (corr.).

0.1602 gram substance gave 0.3117 gram CO_2 and 0.0720 gram H_2O.

	Calculated for $C_{10}H_{11}NO_8$.	Found.
C	53.31	53.08
H	5.39	5.62

Acetone Dicarboxylic Acid.

2,6-Dicarboxy-4-nitrophenol, $C_8H_5NO_7.H_2O$.—Acetone dicarboxylic acid condenses rapidly with nitromalonic aldehyde in neutral or feebly alkaline solution, and after the lapse of a few minutes the addition of hydrochloric acid causes the separation of fine silky needles of the nitrooxyisophthalic acid which is thus formed. The acetone dicarboxylic acid used was prepared according to the directions of v. Pechman[1] and recrystallized from warm water. It was dissolved in a slight excess of sodic hydrate, 2.25 molecules, one molecule of sodium nitromalonic aldehyde added and the deep orange-yellow solution sharply acidified with hydrochloric acid after the lapse of twenty-four hours. The weight of the product thus obtained amounted to 90 per cent of the theoretical yield, and it could readily be purified by recrystallization from hot water. The acid then crystallizes in finely felted, colorless needles which contain one molecule of water of crystallization; it slowly loses in weight at 100°, but rapidly at higher temperatures.

1.1890 gram substance lost 0.0882 gram H_2O at 100°.

	Calculated for $C_8H_5NO_7.H_2O$.	Found.
H_2O	7.35	7.42

The acid dried at 100° then gave the following results:

I. 0.2186 gram substance gave 0.3398 gram CO_2 and 0.0537 gram H_2O.

II. 0.2224 gram substance gave 0.3468 gram CO_2 and 0.0528 gram H_2O.

III. 0.2288 gram substance gave 13.3 cc. moist nitrogen at 25° and under a pressure of 749 mm.

	Calculated for $C_8H_5NO_7$.	Found. I	II	III.
C	42.28	42.39	42.53	
H	2.22	2.75	2.66	
N	6.18	....	....	6.53

1. Ann. Chem. (Liebig), **261**, 155.

This nitrooxyisophthalic acid is readily soluble in alcohol, sparingly soluble in ether, and almost insoluble in chloroform or benzol; it dissolves freely in hot glacial acetic acid or in hot water. The anhydrous acid melts at 213°–214° (corr.), the hydrous acid about 20° lower, but since the latter begins to lose its water of crystallization at 100°, this melting-point can not be sharply determined. The primary sodium salt is nearly colorless, and very sparingly soluble in cold water, though readily soluble in hot water; it crystallizes in slender, felted needles, which may easily be mistaken for the acid. The secondary sodium salt is pale yellow and quite readily soluble in cold water. The tertiary sodium salt is also readily soluble, but is deep orange-yellow in color. The color of the tertiary salt may be used as an indicator in the titration of the acid, as already noted by Schiff[1] in the case of the basic sodium salt of nitrosalicylic acids.

0.2369 gram hydrous acid required 19.40 cc. tenth-normal sodic hydrate.

	Calculated for $C_8H_5NO_7.H_2O$.	Found.
2 NaOH	19.33	19.40

When a hot aqueous solution of the acid is added to a hot solution of argentic nitrate a crystalline silver salt is at once thrown down in the form of finely felted, pale yellow needles. When well washed with hot water and dried in a desiccator this proved to have essentially the composition of a secondary silver salt.

0.2708 gram of the salt gave 0.2280 gram AgBr.

	Calculated for $C_8H_3NO_7Ag_2$.	Found.
Ag	48.95	48.37

When heated with concentrated hydrochloric acid under pressure at 180°–200° the nitrooxyisophthalic acid was slowly broken up. Carbonic dioxide was formed, but it was not found practicable, at least on a small scale, to isolate among the products formed the corresponding nitrosalicylic acid. Fuming nitric acid, however, attacked the acid at 100° with the evolution of carbonic dioxide. On evaporation and recrystallization of the residue from hot water, picric acid was

[1] Ann. Chem. (Liebig), **198**, 265.

obtained in abundance; it melted at 121°–122° and gave the characteristic potassium salt. Evidently the two carboxyls had thus been directly replaced by nitro groups.

CXX.—FERROUS IODIDE[1].

By C. Loring Jackson and I. H. Derby.

The accounts of anhydrous ferrous iodide which we have been able to find in the chemical literature are very contradictory. Serullas[2] seems to have been the first to obtain it by the rather strange method of passing iodine and steam through a red-hot iron tube filled which charcoal. He describes it as shining yellow crystals looking like gold filings. Gay Lussac and Davy[3] say it is a brown mass which fuses at a red heat and sublimes at a higher temperature. A. T. Thomson[3] treated one part of iron with two of iodine suspended in water, and after evaporating off the water in a flask containing some free iron, obtained a steel gray laminated mass melting at 177° and possessing a sharp puckery taste. When heated in air it left a residue of ferric oxide. In 1861 Carius and Wanklyn[4] prepared it as a gray laminated mass by heating iron filings and iodine in a porcelain crucible. In 1863 De Luca[5] states that Faville had made it under his direction, and that it is a pure white amorphous powder. He gives no statement of the method of preparation in any of the journals which are accessible to us. Finally Erdmann[6] in his Lehrbuch (1898) describes it as a reddish-brown body, also without giving the method of preparation. The color of ferrous iodide, therefore, is not by any means settled, the balance of evidence in the chemical literature being in favor of gray or white; but as no analyses of the anhydrous salt have been published, so far as we can find, none of the statements quoted above can be considered to rest on a solid foundation. Under these circumstances it seemed worth while to take up the

1 Presented to the American Academy of Arts and Sciences, May 10, 1899.
2 Gmelin-Kraut, Handbuch, III, 350, 6th edition.
3 Pharm. J., **1**, 44 (1842).
4 Ann. Chem. (Liebig), **120**, 69.
5 Compt. rend., **55**, 615.
6 Lehrbuch der anorganischen Chemie, 62.

study of ferrous iodide and the results of our work in this field are contained in the following paper.

Preparation of ferrous Iodide.

The method adopted consisted in passing the vapor of iodine over heated iron. In the first experiments a combustion tube was used with a stream of carbonic dioxide to carry the iodine, but as we found a temperature above the softening point of hard glass was necessary, we replaced the glass tube with one of iron, which we heated with a Fletcher's tube furnace. At the high temperature thus obtained the iron was oxidized by the carbonic dioxide, and the film of oxide thus formed protected the metal from the action of the iodine; accordingly the carbonic dioxide was replaced by nitrogen, after which good results were obtained.

The apparatus in its final form consisted of two large bottles, which served as gas holders for the nitrogen, and were united by glass tubes and rubber connectors in such a way that, by letting in water from the water works, the gas could be forced out of one of them at a regulated rate through the purifiers and the iron tube to the other bottle, in which it was collected. When this was full of gas, by a simple rearrangement of the pinch-cocks, the nitrogen could be forced back through the apparatus again in the same direction as before into the first bottle. By means of this device the same nitrogen could be used over and over again, thus causing a great saving in time and labor. The nitrogen was made by the excellent method of Dr. Gibbs,[1]—equal parts of sodic nitrite, ammonic nitrate, and potassic dichromate were pulverized, and mixed with three parts of water in a flask with a wide delivery tube. The gas came off when the mixture was gently warmed. Twenty-four grams of the mixture gave about 1200 cc., of nitrogen. The nitrogen, after leaving the gas holder, was purified by passing through a solution of sodic hydrate, sulphuric acid, and a long column of calcic chloride, after which the oxygen was removed by means of a layer of finely divided copper heated in a tube of hard glass by means of a kerosene stove. This precaution was necessary, as the nitrogen was

[1] Ber. d. chem. Ges., 10, 1387.

contaminated with air introduced when the tubes were opened, or from the water in the gas holders. We tried at first an alkaline solution of pyrogallol for the removal of the oxygen, but as we found this was not efficient, we resorted to the layer of finely divided copper, which was prepared by reducing cupric oxide.

The reaction took place in three steel bicycle tubes, the largest of which was one inch (2.54 cm.) in outside diameter and about one-sixteenth of an inch (1.59 mm.) thick. The other tubes were somewhat thinner and small enough to slip tightly into the larger tube. The larger tube contained the iron, which was used in the form of wire clippings (card teeth), as it was found by experiment that these gave a better yield of iodide than turnings, filings, or iron by hydrogen. The iron was freed from organic matter by heating it in a stream of hydrogen before using it. The layer of iron in the tube was about 23 cm. long, and this portion of the tube was heated directly by the Fletcher furnace to a bright red heat. One of the smaller tubes was slipped into the larger one at its end nearest the gas holder containing the nitrogen, in this was placed the iodine, which was slowly volatilized by the heat conducted along the iron tube, and the vapor thus formed was swept over the hot iron in the furnace by the stream of nitrogen; this tube was connected with the purifiers by a perforated cork and glass tube far enough from the heat to avoid danger of burning. It was fouud wise to protect this cork from the iodine vapor, some of which crept back even against the current, by an asbestos or iron diaphragm. The second smaller iron tube was slipped into the further end of the larger tube, and reached the heated portion of it, so that the vapor of ferrous iodide formed in the larger tube condensed in the smaller one, from which it could be easily collected by withdrawing this smaller tube after it had cooled in the atmosphere of nitrogen. The joints of the iron tubes were rendered air tight by means of large rubber connectors, which were kept cool by winding them with lamp-wicking that dipped into a beaker of water. The receiving tube just described was connected with some bottles of strong sulphuric acid to prevent the creeping back of any aqueous vapor into

the tube. The delivery tube from these bottles conveyed the nitrogen to one of the gas holders already described.

In carrying on the process it was observed that a considerable amount of iodine was taken up by the iron before any iodide distilled over; but after it began to appear, it continued to collect for several hours, so that the yield was a good one, and when the apparatus has been once set up the ferrous iodide can be obtained in quantity with little trouble.

As the product of the reaction just described had a deep red color in thin plates, and looked almost black when the mass was even moderately thick, we supposed at first that it could not be a ferrous salt, and accordingly applied the following tests. A little of it treated with water, in which it dissolved completely and with great ease, gave no color with a solution of potassic sulphocyanate, but a strong test for a ferrous salt with potassic ferricyanide. As it was possible that it might be a ferric iodide which was decomposed by water into the ferrous salt and free iodine, we next tested for iodine both with starch paste and with carbonic disulphide, but with negative results. These qualitative experiments indicated that the substance, in spite of its red color, was ferrous iodide; and that this is the case was proved by the following analyses. The substances used in I.–V. and in IX. and X. were the direct product of the reaction. In VI., VII., and VIII., this product had been purified by sublimation before it was analyzed.

I. 0.6717 gram of substance gave 1.0202 gram of AgI and 0.1720 gram of Fe_2O_3.

II. 1.0400 gram of substance gave 1.5736 gram of AgI.

III. 0.9658 gram of substance gave 1.4601 gram of AgI.

IV. 0.7493 gram of substance gave 1.1471 gram of AgI and 0.1934 gram of Fe_2O_3.

V. 0.8327 gram of substance gave 1.2586 gram AgI and 0.2209 gram of Fe_2O_3.

VI. 1.2675 gram of substance gave 1.9232 gram of AgI and 0.3261 gram of Fe_2O_3.

VII. 0.7396 gram of substance gave 1.1192 gram of AgI and 0.1932 gram of Fe_2O_3.

VIII. 0.5944 gram of substance gave 0.8978 gram of AgI.

IX. 0.3831 gram of substance gave by ignition 0.0982 gram of Fe_2O_3.

X. 1.7526 gram of substance gave by ignition 0.4658 gram of Fe_2O_3.

Calculated for		Found								
	FeI_2	I.	II.	III.	IV.	V.	VI.	VII	VIII.	IX.	X.
I	81.92	82.10	81.77	81.74	82.71	81.66	82.00	81.76	81.64	....	....
Fe	18.08	17.92	....	....	18.07	18.56	18.01	18.28	....	17.94	18.60

Of these analyses I.—VIII. were made by passing sulphurous anhydride into the aqueous solution to convert any free iodine (formed by the action of air on the solution) into hydriodic acid, and to dissolve the ferric hydrate, if any, formed at the same time as the free iodine; then, after driving off the excess of the sulphurous anhydride, the iodine was precipitated as argentic iodide and the iron as ferric hydrate in the usual way. Analyses IX and X., were made by simple ignition of the ferrous iodide in a porcelain crucible, when it loses all its iodine and is converted into ferric oxide.

Properties of Ferrous Iodide.

The anhydrous salt prepared as described above forms plates of a deep full red color with a slight brownish tint. This color is a much more pronounced red than any appearing among the ferric salts with the exception of ferric sulphocyanate. In thicker masses it is nearly or quite black; when melted and allowed to solidify, it forms a blackish-red crystalline mass, which looks brown on a surface of fracture.[1] When the plates are examined under the polarizing microscope, they give evidence that they belong to one of the uniaxial systems, but the outlines of these crystals are so ragged that they furnish no means of deciding to which system they belong. Accordingly some of the plates immersed in ether, in which they dissolve very slowly, were observed under the microscope, when the formation of regular hexagonal holes was observed; there is no doubt, therefore, that the crystals belong to the hexagonal system. If the salt is resublimed

[1] The dark color of the ferrous iodide is not without analogy, as G. P. Baxter has found in this laboratory that ferrous bromide has a dark yellow color with a greenish-brown tinge.

slowly, it can be obtained in broad, thin plates with a brilliant vitreous lustre; but on one occasion very small yellow plates were formed which called to mind the "gold filings" of Serullas. The melting-point of the substance is given by Thomson at 177°; we have not attempted to determine this point anew, as it seemed to us of little practical value on account of the very deliquescent nature of the salt. If heated to about the fusing point of soft glass in an inert gas it sublimes essentially unaltered. When sublimed in a stream of nitrogen, part of the iodide is deposited in the red plates already described, the rest is carried on further in the tube as a yellow cloud, which deposits a dark reddish-brown amorphous powder; this is found to be much more susceptible to the action of atmospheric moisture than the red plates, but we think this difference in behavior is due only to the difference in the size of the particles in the two specimens. The sublimation may take place in nitrogen, carbonic dioxide, or even hydrogen, but oxygen must be carefully excluded, as this decomposes the iodide rapidly at not very high temperatures, so that on gently heating a sample of it in a porcelain crucible in a few minutes all the iodine has passed off in violet fumes, and there is left a reddish-brown residue of ferric oxide, which retains the shape of the crystals of the ferrous iodide, and is magnetic. That this latter property was not due to the presence of some magnetic oxide or metallic iron in the residue was proved by dissolving it in hydrochloric acid, when a strong test for ferric chloride, but none whatever for ferrous chloride, was obtained. The iodine is so completely removed by this ignition in air that the process was used as a method of analyzing the ferrous iodide (Analyses IX. and X.). De Luca observed a similar decomposition of his (white) ferrous iodide. The same decomposition of the ferrous iodide by the oxygen of the air takes place slowly at ordinary temperatures; a specimen of it kept in a good desiccator gives off enough iodine vapor in time to color the air within the desiccator a distinct purple. A sample of the salt was kept in a desiccator over potassic hydrate, to absorb the iodine, for thirteen months, and the decomposition followed by occasional weighings, when it was found that about seven-eighths of the total

loss of iodine, was given off in the first six months, but that even at the end of thirteen months the decomposition was not complete, as the residue still contained a little iodine, and gave tests for both ferrous and ferric compounds. It follows from these observations that the salt should not be allowed to stand even in a desiccator before analysis, but should be analyzed as soon as possible after its preparation.

If the salt is exposed to the atmosphere, it deliquesces quickly to a brown solution. The thinner plates, when kept in a corked flask or a desiccator, behaved in a very striking way; the red plate showed at first a white border around its edge, which gradually spread inward, until the whole plate became white; this change was soon followed by a liberation of iodine, which imparted a gray or even black appearance to the mass. The appearance of the iodine is undoubtedly due to the decomposition by air just described, but the cause of the whitening of the crystals was not so evident. The most obvious theories were, that the white substance was a second modification of the ferrous iodide, or that it was produced by the absorption of water, which might either form enough of the green ferrous iodide containing four molecules of water of crystallization to neutralize optically the red color of the anhydrous salt, or might give a definite compound containing less water of crystallization than the green salt. The idea that the white substance was a second modification gained some support from the observations of Thomson, Carius and Wanklyn, and De Luca, who describe ferrous iodide as white or gray, and also from the fact that the white compound was formed in atmospheres containing very little water, although in none of these cases had moisture been rigorously excluded.

We, therefore, tried a number of experiments to settle this point. In all these it was necessary to select specimens of the salt which show this change from red to white, such as rather thin red plates or the brown amorphous powder obtained by sublimation, since thicker plates or masses of the iodide show the phenomenon with difficulty or not at all. We see no reason, however, to ascribe these differences in behavior to anything except the size of the crystals. Two similar portions of the ferrous iodide were exposed, the one to dry

carbonic dioxide, the other to moist carbonic dioxide, the experiments being carried on at the same time and under parallel conditions. The specimen in the moist gas turned white quickly, while that in the dry gas remained unaltered. Other similar experiments showed that the change of color took place much more slowly in a gas containing little moisture than in one containing more. In all these experiments the amount of moisture must be kept small, as, if too much aqueous vapor is used, the salt deliquesces so rapidly that the formation of the white body cannot be observed. A sample of ferrous iodide was immersed in absolute ether (dried with sodium) and underwent no change of color even after long standing; when, however, a minute fraction of a drop of water was added, it rapidly turned white. Upon heating a specimen of the white body in a tube filled with dry carbonic dioxide a cloud appeared which looked like moisture and condensed in the cold part of the tube, the substance turning red at the same time. As the tube cooled this moisture was quickly reabsorbed, and the white body was formed again. This experiment was repeated several times with the same specimen. These experiments leave no doubt that the white substance is not a second isomeric modification of the ferrous iodide, but is formed by the action of water on the red anhydrous salt.

The question next arises, is the white body a mixture of the red anhydrous and the green hydrous ferrous iodide, or is it a crystallized salt with a definite amount of water? Our experiments are not sufficiently conclusive to answer this question with certainty, but we would present the following argument in favor of the second view with all necessary reserve. A sample of ferrous iodide was exposed at ordinary temperatures (in this case about 22°) to an atmosphere of hydrogen kept moist by contact with dilute sulphuric acid containing 33 per cent of acid, and the absorption of water followed by successive weighings at intervals of about a day. Upon plotting these results a curve was obtained, which showed a change in the rate of absorption at a certain point, and a calculation of the amount of water absorbed at this point gave the following result:

0.4289 gram of ferrous iodide absorbed 0.0491 gram of water.

	Calculated for $FeI_2 2H_2O$.	Found.
H_2O	10.40	10.28

The coincidence of these numbers is certainly striking, and, so far as it goes, tells in favor of a definite composition for the white body; but little weight can be given to a single determination, and in this case the result must be regarded with the more suspicion, because the ferrous iodide, after it had turned from red to white in this experiment, became gray from decomposition with liberation of iodine.

When one of the red plates was viewed under the polarizing microscope in ordinary air, it appeared at first granular and then white, at the same time assuming a lower order of symmetry, as extinction was observed at certain angles when the stage was rotated, an effect which could not have been produced by the original crystal, as it was a hexagonal plate bounded by two basal planes. This observation shows little more than that the white substance was crystalline.

The anhydrous ferrous iodide dissolves rapidly and freely in water with a considerable evolution of heat. The dilute solutions are colorless, the stronger ones green. The hot saturated solutions deposit green crystals of $FeI_2 4H_2O$. Our analysis of this salt gave results which agreed only approximately with those required by the theory, but this is not strange, as it is very deliquescent and rapidly decomposed by the oxygen of the air with liberation of iodine. The water cannot be determined by loss, as the salt gives off hydriodic acid when it is heated. Fortunately it was not necessary for us to spend our time in attempting to obtain better analytical results, as Volkmann[1] has made a careful study of crystallized ferrous iodide, and has isolated it with four, six, or nine molecules of water of crystallization. From his description of the preparation of these salts there can be no question that the salt obtained by us was $FeI_2 4H_2O$.

The solution of ferrous iodide, when exposed to the air, is decomposed, turning at first brown and then throwing down a yellowish-brown precipitate of ferric hydrate or a basic

[1] Ber. d. chem. Ges., 27, R. 618.

ferric salt; iodine is set free at the same time, and apparently some hydriodic acid is also formed.

The ferrous iodide is very susceptible to the action of oxidizing agents, as appears from the account given above of the action of air on it at ordinary temperatures, but it shows a very striking resistance to the action of reducing agents. Its behavior in this respect was studied with some care in the hope of perhaps encountering a subiodide. As has been already stated, ferrous iodide can be sublimed essentially unaltered in an atmosphere of dry hydrogen. This is not perhaps altogether unexpected, as it has been found in this laboratory that cobaltous bromide is only partially reduced when heated in dry hydrogen, the remainder subliming unaltered, while nickelous bromide was reduced under the same conditions essentially without sublimation.[1] When hydrogen was passed through melted ferrous iodide, no more reduction was obtained. Ferrous iodide, sublimed through a layer of iron by hydrogen, remained unaltered. Mercury alone or when emulsified by grinding with diatomaceous earth produced no effect on ferrous iodide even when distilled with it. When melted with molecular silver, on the other hand, the reduction to metallic iron was complete. Reductions in the moist way with hydriodic acid and iron by hydrogen or zinc dust also seemed to give negative results.

C. Liebermann and H. Sachse,[2] and also P. Bruck,[3] have recommended ferrous iodide as a useful carrier in adding iodine to derivatives of acetylene, such as phenylpropiolic acid, acetylenedicarboxylic acid, or propargylic acid. We have also tried some experiments on the behavior of ferrous iodide with organic compounds, but as the results are of little interest, we shall summarize them as briefly as possible. Ferrous iodide, when heated to redness in ethylene, was reduced, leaving a magnetic residue containing carbon. With acetylene a very gentle heat was sufficient to start a reaction, which afterward proceeded by itself accompanied by a dull red glow. The products were a volatile, yellow liquid containing much iodine and a voluminous residue consisting

[1] Richards and Baxter: Proc. Am. Acad., **34**, 352.
[2] Ber. d. chem. Ges., **24**, 4112.
[3] *Ibid.*, 4118.

of carbon and very little iron. The fact that the ferrous iodide is reduced by these hydrocarbons, when it is almost unaffected by hydrogen, is remarkable. Isopropyl alcohol heated with ferrous iodide gave a little of an insoluble oil, probably the iodide. When treated with an ethereal solution of aniline, the ferrous iodide formed a white compound much more voluminous than the original salt; this, in all probability, is an aniline addition product analogous to the ammonia compound described later. Benzol, benzyl chloride, ether, phenol, or hydroquinone gave no perceptible action with ferrous iodide.

Other Methods of Preparing Ferrous Iodide.

In this section of the paper we shall describe a revision of the methods used by our predecessors, and also some new methods of our own.

The revision of the older methods was necessary, because in three case the ferrous iodide formed was described as gray or white; and although we have proved that the white samples formed from the red salt owed their change of color to absorption of water, it did not follow that those described by our predecessors were not anhydrous ferrous iodide in a second isomeric form. De Luca,[1] who states that ferrous iodide when pure is white, gives no method of preparation in any of the journals to which we have access, so that it was impossible for us to repeat his work. A. T. Thomson[2] prepared his gray ferrous iodide by evaporating an aqueous solution in a flask containing some free iron. On repating this experiment we had so much difficulty from oxidation that we carried on our later attempts in an atmosphere of carbonic dioxide. Under these conditions, when the water of crystallization began to come off, the liquid became black and opaque-looking as if it contained a suspended black precipitate. Later the surface of the boiling mass became grayish white with a silvery lustre, but when all the water had been driven off, the residue was brownish-red like the ferrous iodide prepared by our method. This experiment makes it probable that the gray ferrous iodide of Thomson owed its

[1] Comptes rendus, **55**, 615.
[2] Gmelin-Kraut: Handbuch, III, 350, 6th edition.

color to the presence of water, for in the absence of analyses he would undoubtedly have ascribed the brownish-red color of the final residue to the formation of a ferric salt by oxidation.

As the method of Carius and Wanklyn[1] consisted in heating iron and iodine in a porcelain crucible, it seemed at first sight that the gray color of the product could hardly be due to the presence of water, and therefore we repeated their work, following their directions as carefully as possible. One gram of rather coarse iron filings,[2] mixed with a little iodine to drive out the air, was heated in a covered porcelain crucible to redness as quickly as possible; four grams of iodine were then added in two portions, and the heating continued until comparatively little iodine vapor escaped around the edges of the cover. When cool, the product was found to be a fused mass, consisting, after it had been broken out of the crucible, of red scales exactly like those described earlier in this paper. These scales upon exposure to the air soon turned grayish-white, and then deliquesced to a brown solution. We have repeated this process of Carius and Wanklyn many times, and in every case the ferrous iodide formed has appeared in red scales, before it had been exposed to the air long enough to absorb moisture. We, therefore, are compelled to ascribe the gray color mentioned by Carius and Wanklyn to the absorption of water from the air, since they, like Thomson, would in the absence of analyses have supposed that the red color was due to oxidation. Our present knowledge, therefore, gives no reason for supposing that anhydrous ferrous iodide has any other color than red.

Another method of preparation may be described here, as it was tried to see whether a white form might not be obtained at comparatively low temperatures. A small quantity of iron by hydrogen was placed in the middle of a small glass tube, and secured by two plugs of asbestos; an excess of iodine was inserted in one end of the tube, which was then filled with nitrogen and sealed at both ends. The end containing the iodine and iron was then heated to 120° by means of an air-

[1] Ann. Chem. (Liebig), **120**, 69.

[2] The success of the process depends on using filings of the right degree of coarseness. With too fine or too coarse filings unsatisfactory results are obtained.

bath, and after most of the iodine had sublimed into the cold upper part of the tube, it was reversed so that this end and the iron were heated to 120°. After repeating this distillation of the iodine through the iron several times, all the metal was converted into the red ferrous iodide. This is a good method for preparing a specimen to be kept to show the color. Ferrous iodide was also made by passing hydrogen and iodine vapor over heated ferric oxide.

Of these methods of preparation, that of Carius and Wanklyn is the easiest, but it gives a product apt to be contaminated with metallic iron and oxide of iron. Thomson's method is tedious, and does not give a pure product, as we observed evolution of hydriodic acid toward the end of the evaporation even in an atmosphere of carbonic dioxide. The sealed tube method is also slow and imperfect, so that the best method, if the pure salt is desired, is the heating of iron and iodine in nitrogen given in the first part of this paper.

Action of Ferrous Iodide with Ammonia.

When anhydrous ferrous iodide was exposed to a stream of ammonia gas at any temperature between 0° and 100° a large amount of the gas was absorbed, and the iodide was converted into a voluminous white powder. The composition of this substance was determined by finding the increase in weight during the treatment with ammonia.

I. 3.5507 grams FeI_2 gained 1.1701 grams of NH_3.

II. 2.5411 grams gained 0.8449 gram of ammonia.

	Calculated for $FeI_2 6NH_3$.	Found. I.	Found. II.
NH_3	24.76	24.78	24.95

The substance therefore corresponds in formula to the compound $FeCl_2 6NH_3$ made from ferrous chloride under the same conditions.

Properties of the Hexammonia Ferrous Iodide.

It forms a pure white amorphous powder, which occupies many times the volume of the ferrous iodide from which it is made, and has a very low specific gravity. Water decomposes it at once with a considerable rise of temperature; the products are ferrous hydrate, ammonic iodide, and ammonia.

We did not succeed in finding an organic solvent for it. When exposed to the air it gives off ammonia rapidly and turns brown; in an atmosphere of ammonia it remains unaltered even at 100°; heated in an indifferent gas it loses ammonia, and is converted into a dark-brown powder, which seems to be stable in the air. Two analyses indicated that this brown substance contained between two and three molecules of ammonia to each molecule of ferrous iodide. Its stability in air leads us to think that it is a new compound, but evidently it was not pure, as the analyses differed by three per cent. Unfortunately we could find no way of purifying it.

Action of Bromine on Hexammonia Ferrous Iodide.

When the compound $FeI_2 6NH_3$ was exposed to the vapor of bromine, it absorbed a large quantity, so that the product in one case contained 71.03 and in another 70.41 per cent of bromine. This apparent constancy in the amount of bromine absorbed led us to examine the product more carefully in the hope that it might be a definite compound, but our experiments have convinced us that it is only a mixture essentially made up of ferric bromide, ammonic bromide, and an ammonic bromiodobromide, NH_4BrIBr. The product had a reddish-brown color, and gave off bromine when exposed to the air. It was investigated by treating it with ether, in which a portion dissolved with considerable evolution of heat. The residue insoluble in ether had a yellowish color, and seemed to be a mixture of ferric bromide and ammonic bromide in varying proportions. These two substances were recognized by the usual tests. The ether extract on evaporation left a residue which was green with a brilliant metallic luster by reflected light, deep blood-red by transmitted light; it resembled rosaniline, therefore, but the red color was less purplish than in that body. Examined with the microscope, crystals which looked like ammonic bromide were observed. It had a strong odor similar to that of bromide of iodine, and, although not really stable, could be kept for some time without much decomposition. Upon treating it again with ether a fresh quantity of the insoluble yellowish residue was left

behind. The residue obtained by evaporating one of our first ether extracts was analyzed with the following results:

0.7149 gram of the substance gave 0.0216 gram of Fe_2O_3, 0.0405 gram of NH_3, and 1.4289 grams of mixed silver salts which yielded 0.7652 gram Ag.

In calculating these results, as the iron from its small amount was evidently an impurity, the amount of ferric bromide corresponding to it has been subtracted from the amount of substance taken, and the bromine contained in this ferric bromide from the bromine found. As the substance gave a test for a ferrous salt, it would have perhaps been more correct to consider the iron present as ferroferric bromide, and this would have given numbers agreeing better with those calculated from the formula; but we think it wiser to give the results on the assumption that ferric bromide was present, and we cannot believe that the amount of ferrous bromide was more than a trace, since the substance had been exposed to an excess of bromine.

	Calculated for NH_4BrIBr.	Found.[1]
NH_3	5.90	6.38
I	41.64	40.96
Br	52.46	53.32

These numbers would seem conclusive if it were not for the presence of the small amount of ferric bromide (considered in calculating them) and the appearance under the microscope of crystals resembling ammonic bromide; but with these sources of error, we thought it necessary to support our analysis with evidence of some other sort, and therefore undertook the preparation of NH_4BrIBr direct in order to compare its properties with those of our compound. Upon treating ammonic bromide with an ethereal solution of bromide of iodine, the salt dissolved, giving a red solution, and on evaporation of the ether a residue was obtained, the properties of which were identical with those of the ammonic bromiodobromide described above. Further, upon exposing ammonic iodide to the vapor of bromine an amount was

[1] If the ferric bromide was not subtracted, the numbers were, NH_4, 5.67; iodine, 36.39; and bromine, 56.41.

absorbed corresponding very nearly to that required by the formula.

1.6487 grams of NH_4I absorbed 1.7804 grams of Br.

	Calculated for NH_4BrIBr.	Per cent. of bromine in the product.
Br	52.46	51.92

During the action of the bromine the ammonic iodide at first turned black, but as the absorption went on it finally became scarlet, and this product proved to be identical with the ammonic bromiodobromide. A curve constructed from the increase of weight of the ammonic iodide showed that there was a marked diminution in the speed of the absorption after the first atom of bromine had been added. This decrease in the speed of absorption is undoubtedly connected with the conversion of the black substance into the red NH_4BrIBr, but we are unable to decide whether this black intermediate product is another compound NH_4BrI, or only a mixture of ammonic bromide and free iodine. It is a curious fact, in view of the absorption of free bromine by ammonic iodide, that so far as we could find, an ethereal solution of bromine had no action on this salt. We have not continued our experiments in this direction for fear of intruding on the field of work occupied by Wheeler, who with Pratt and Barnes has prepared the ammonic triiodide.[1]

We have adopted provisionally the name ammonic bromiodobromide and the formula NH_4BrIBr for this substance, because it is made by the action of bromide of iodine on ammonic bromide, and when it decomposes bromide of iodine is given off and ammonic bromide left behind; but we do not feel that these observations settle its constitution finally, although they certainly are strong arguments in favor of the formula adopted. If this is correct, the formation from ammonic iodide and bromine must be preceded by the replacement of the iodine in the salt by bromine, and this may account for the fact noted above, that an ethereal solution of bromine does not act on ammonic iodide.

Properties of Ammonic Bromiodobromide, NH_4BrIBr.

The salt has a blood-red color in transmitted light, but is a

[1] This JOURNAL, 19, 675.

brilliant green with a metallic luster by reflected light. The specimens examined by us contained very elaborately twinned crystals with the branches at right angles, but we are inclined to think that these consisted of ammonic bromide, which is easily formed by the decomposition of our salt; on this account it smells of bromide of iodine, and on long standing leaves a white residue of ammonic bromide; the same decomposition takes place to a limited extent when it is dissolved in ether; the ethereal solution is dark-red. When treated with water, bromine and iodine are set free, and a solution is formed. Hydrochloric acid sets free, iodine. Sodic hydrate or ammonic hydrate gives a black precipitate of iodide of nitrogen; upon adding hydrochloric acid to the filtrate from this iodide of nitrogen, bromine is set free. Sulphurous acid gives hydrobromic acid and hydriodic acid.

Contributions from the Chemical Laboratory of the University of Oregon.

THE PREPARATION OF ZINC ETHYL.

By Arthur Lachman.

About three years[1] ago I published a brief outline of a method of preparing zinc ethyl. As is well known, the chief difficulty in this preparation is to secure a suitable form of zinc; and this difficulty was overcome by the use of zinc dust, which is both cheap and plentiful. My note, though brief, contained all the information needed for the immediate application of the process; and a more detailed description would be entirely unnecessary, were it not that a zinc dust method[2] has since then been published which does not appear to offer any advantages over the older one. The two methods differ in that Simonowitsch uses zinc dust mixed with filings, whereas my process is to be regarded as a modification of the Gladstone-Tribe method[3] in that it uses an alloy of zinc dust with copper. The method of Gladstone and Tribe has long been recognized as yielding by far the best results; and the only obstacle to its universal employment would seem to be the great difficulty of preparing their "zinc-copper couple"

[1] This Journal, 19, 410 (1897.)
[2] Simonowitsch: Chem. Centrbl., 1899, I, 1066.
[3] J. Chem. Soc., 35, 569.

in large quantities. Part of this difficulty lies in the fact that they use zinc filings for this purpose, for filings are hard to procure in quantity; the chief obstacle, however, is that great manual dexterity is required for the successful alloying of the two metals. Moreover, a number of operations are called for: the filings must be freed from oil, they must be cleaned with acid if appreciably oxidized, and then carefully dried, the copper must be prepared by careful reduction of its oxide, and finally the two metals must be alloyed with such care that only small amounts can be taken at one time. As my method yields unlimited quantities of alloy in a single operation which is automatic and does not occupy more than twenty minutes' time, and as it furnishes an excellent yield of zinc ethyl, it may fairly claim to be an improvement upon its progenitor. The details of the new method proposed by Simonowitsch will be considered by the side of the corresponding details of my own.

1. The Zinc Dust-copper Couple.

Gladstone and Tribe have shown that the best yields are obtained when zinc and copper are alloyed in the proportions of about 9 to 1. Zinc dust contains an average of 90 per cent. of metal, so that the above proportions are approximated if 100 parts of zinc dust are mixed with 12 parts of copper oxide, and then reduced by heating in a current of hydrogen.

100 parts zinc dust and 12 parts copper oxide (in the finest possible powder[1]) are thoroughly mixed and placed in a long glass tube. This tube, which may be of soft glass, should be as wide as the channel of a combustion furnace will permit; at distances corresponding to the length of the channel it should be narrowed to about half its diameter. A plug of glass wool is fitted into one constriction, the tube then filled about one-half full, and a plug inserted into the other end. The tube is now shaken and rotated in a horizontal position until the mixture spreads out in an even layer. A moderate current of dry hydrogen is then passed through the tube, and the latter heated in the furnace. It is not a difficult matter

[1] This is a commercial article.

to properly regulate the heating, a flame of about 5 to 10 cm. being needed according to the construction of the furnace. The only essentials are to heat the whole tube at once, to rotate the tube one quarter turn at an interval of a few minutes, and not to be afraid of heating too strongly. It has succeeded best when the powder has slightly baked together, and must be dislodged by a stout wire. Reduction is complete within twenty minutes from the start. The alloy looks much lighter than the mixture and is considerably coarser, though still a fine powder. The contents are allowed to cool in hydrogen (best by removing the tube from the furnace), and are shaken out when no longer hot to the touch. It is advisable to use as soon as possible, though I have kept the alloy several days in an ordinary glass-stoppered bottle without noticeable deterioration.

It will be seen that this method is much more expeditious than the one given by Simonowitsch. The latter first cleans the zinc dust with dilute acid, washes, and finally dries it in a current of carbon dioxide at a definite temperature. This prepared dust must then be mixed with a considerable proportion of dry, clean filings. It has already been pointed out that filings are hard to obtain.

2. *First Stage of the Zinc Ethyl Synthesis.*

The action of zinc upon ethyl iodide, as is well known, proceeds in two entirely distinct phases. The first consists in a direct addition of ethyl iodide to zinc:

$$Zn + C_2H_5I = Zn\begin{matrix} I \\ C_2H_5 \end{matrix}$$

It is carried out at the temperature of the water-bath, and its completion becomes manifest by the disappearance of the ethyl iodide. It is customary to carry out this reaction with a great number of complications, such as a mercury valve for increasing the pressure as well as the boiling-point of the liquid (Simonowitsch uses this device), a current of dry hydrogen for keeping out the air, etc. But these are all unnecessary. Equal parts of alloy and ethyl iodide are simply placed in a flask connected with a long reflux con-

denser, and the mixture kept *gently* boiling on the water-bath until no more ethyl iodide drops back. Violent boiling may drive some of the liquid through the condenser. The time varies from thirty to sixty minutes, according to circumstances that cannot be rigorously defined. I have found it preferable to work with small quantities at a time (from 150-250 grams each of alloy and iodide), to use an Erlenmeyer flask of about 500 cc. capacity, and to take pains to spread the alloy in a thin, even layer on the bottom. The speed of reaction seems to depend on the surface of metal exposed;[1] and this would appear to be the reason why Simonowitsch introduces zinc filings into his flasks.

It is a curious fact that the longer the time required for completing this reaction, the more does a secondary process take place, resulting in the formation of butane and consequent loss of zinc ethiodide:

$$2C_2H_5I + Zn = (C_2H_5)_2 + ZnI_2.$$

This is an additional reason for desiring rapid action. Once the ethyl iodide is all used up, the process can be indefinitely interrupted at this point, if not convenient to proceed to the final stage.

3. Second Stage of the Synthesis.

The conversion of zinc ethiodide into zinc ethyl according to the equation:

$$2C_2H_5ZnI = Zn(C_2H_5)_2 + ZnI_2$$

is accomplished by heating to 180°–220°. The flask containing zinc ethiodide is fitted with a double-bored cork, through which connection is made with a condenser and with a generator furnishing dry carbon dioxide. The current of gas should be moderately rapid at first, very slow during distillation, and rapid again at the end in order to wash out the remaining few cubic centimeters in the flask. The zinc ethyl should be purified by redistillation, as it invariably contains a small amount of unchanged ethyl iodide; for this reason a distilling flask of suitable size should serve as a receiver, to avoid subsequent transfer. The heating is best accomplished

[1] During the boiling little or no liquid penetrates through a thick layer of the powder.

in an oil-bath. In my former note I recommended the use of asbestos air-baths as being cleaner and more expeditious; but this advantage is more than offset by the occasional bursting of a flask at the height of the distillation. Fifteen or twenty minutes suffice for this operation.[1]

The redistillation of zinc ethyl may be conducted with little trouble as follows: The distilling flask is carefully connected with a condenser; the receiver, which should be a stout Erlenmeyer flask, is filled with carbon dioxide, and fitted to the condenser with a cork from which a good-sized wedge has been removed. A current of carbon dioxide is now delivered almost at the surface of the liquid, and continued until all of the air has been expelled from the apparatus. It is desirable to fit the tube into the flask with a cork, and make the gas escape at the receiver. The gas-jet is now replaced with a thermometer already fitted to a cork, and the distillation carried out as with ordinary liquids; a free flame may be used with perfect safety. All flasks to be used as receivers must be filled with carbon dioxide, and fitted with good, sound corks. To change receivers, fasten the carbon dioxide jet used above so as to play a strong current upon the mouth of the first receiver, gently disengage this from the wedge-shaped cork, and then quickly change flasks, *devoting attention primarily to the new receiver;* the old one may be left with impunity for several minutes, if necessary, before being corked.

4. The Preparation of Zinc Ethyl in Quantity.

The process just outlined applies to a single flask of say 200 grams charge, which will yield on an average 60-70 grams zinc ethyl. The time required for all operations except redistillation is at most one and one-half to two hours, usually not much more than one hour. The method is peculiarly advantageous, however, when it is desired to prepare several hundred grams at one time. I have already mentioned that the yields are better if not more than 250 grams be employed in a single operation; but by judicious planning it is not difficult to prepare practically unlimited

[1] The *total* time required is one and one-half hours. Simonowitsch needs two to two and one-half hours, not including the time needed for preparing the metal.

quantities in a single working day. For this purpose select from three to six flasks of the same aperture, so that all fittings shall be interchangeable. Begin operation by preparing a tubeful of alloy (my tube will hold about 350 grams). While this is heating, mount two condensers in connection with water-baths, and prepare the corks. As soon as the alloy is ready, charge two flasks and prepare more alloy. As these processes require almost no attention, employ the interval to fit up the condenser, oil-bath, and fittings for the second heating. As soon as a flask is ready, wipe it dry, and heat in the oil-bath (which may be warmed to about 110° or even more); then place a third charge upon the water-bath, etc. By these alternations, little or no time is lost, and employing three condensers as described, about 75 grams per hour will be obtained for each hour after the first (*i. e.*, 75 grams in two hours, 150 grams in three hours, etc.). Of course, any greater number of baths and condensers may be employed, if room and assistance permit. I have always worked alone, and have had plenty of spare time working as above.

5. The Manipulation of Zinc Ethyl.

The peculiar property possessed by zinc ethyl of rapidly heating itself to the kindling point in air, naturally renders caution necessary when making use of it. In the last few years I have had occasion to handle several kilos of the substance, and have avoided all mishaps by very simple precautions. On the other hand, the very elaborate appliances which have been devised and recommended for this purpose are very likely to deter many from employing this classic synthetic reagent. I may therefore be permitted to summarize my experiences in this direction.

In the first place, all vessels which are to contain zinc ethyl must be filled with dry carbon dioxide. For drying purposes I use a long tube filled with calcium chloride, and two Muencke wash-bottles containing sulphuric acid. The vessels must be kept corked until used. Secondly, as has been demonstrated by Frankland, caoutchouc stoppers and connections must be avoided, and nothing but dry, sound corks

exposed to the vapor of zinc ethyl. Thirdly, the transfer of zinc ethyl is greatly facilitated by pouring it from Erlenmeyer flasks which have perfectly straight sides; and these flasks must be strong enough to withstand sudden and energetic corking. It is inexpedient to attempt the isolation of definite quantities of the reagent; it is much better to pour out the amount needed approximately, and to suit the amounts of other substances to this. The amount taken is given by the loss in weight of the stock vessel; this is not a very accurate procedure, but answers all practical purposes. Fourthly, zinc ethyl may be poured from one vessel to another with perfect safety if the operation is carried out under an inverted funnel of from 4 to 6 inches in diameter, through the stem of which a rapid current of carbon dioxide is passing. After pouring, the first care belongs to the storage vessel; the other readily takes care of itself for some time. This simple expedient does away altogether with the "assistant"[1] usually deemed indispensable when handling zinc ethyl. Finally, everything likely to be needed should be ready in advance, so that no time need be lost. It not infrequently happens that the carbon dioxide generator gives out at a critical moment. I make it an invariable practice to have two on hand, so that the second one may be coupled up without delay.

The chief inconvenience in the preparation of zinc ethyl is the cleaning of apparatus after it is all over. It therefore pays to make up as much as possible at one time. If not needed at once, I keep it in flasks of about 200 cc. capacity, which are about half filled; these are tightly corked, and kept for safety in a large, lead-lined box with metal cover. The substance has been stored this way for months at a time, with no trouble and with practically no loss by oxidation.

6. Experimental Results.

The following tables will give the data for all the preparations of which I have kept a record; they are not selected, but include the poorest as well as the best I can find in my note-book:

[1] Meyer-Jacobson: "Organic Chemistry," Vol. I, p. 284.

Velocity of First Stage.

Amount of each reagent taken, in grams.	Time in minutes for disappearance of ethyl iodide.
150	50
150	48
200	45
300	65
75	30

Complete Data.

Iodide used in grams.	No. of separate charges.	Time for completion in hours.	Yield.	Theory.
650	7	4	216	256
300	2	2	95	108
1300	13	10	420	512
500	3	2.5	165	195

These experimental results bear out the claim that the method is quick, certain, and efficient. They correspond to a total yield of 84 per cent in the preparation of nearly one kilogram. It should be remarked that in no case was an attempt made to hurry, and that usually I was at the same time busy with other work.

7. The Recovery of Iodine.

The recovery of the iodine which serves as a carrier of energy in this preparation is an exceedingly important affair from the standpoint of laboratory finance. The following method is the one I have found best after many trials:

After heating in the oil-bath, the contents of the flasks form a solid cake. This is broken up with a sharp stick while still warm (it should be remembered that the contents are more valuable than the flask), and dropped into a bucket of water. After standing over night, the liquid is decanted, and the residue washed with water three or four times. A large bulk of liquid is an advantage. The solution is well mixed, and the amount of iodine determined either by analysis or by computation if the quantity of original ethyl iodide is known. After distributing the liquid among several large flasks, which should not be more than half full, add to each the calculated amount of potassium chlorate necessary to free all the iodine, and an excess of commercial hydro-

chloric acid. After an hour or more all the iodine will have settled; if the liquid should grow very warm, which happens when it is too concentrated, cool by standing in water. Decant the acid fluid, wash twice with water, and filter the iodine on a Buchner "nutsche." Press the pulp down hard with a pestle, and draw air through it for several hours.

The iodine thus prepared is by no means dry, but it can be easily used for making ethyl iodide. For this purpose, use as many cubic centimeters of ordinary alcohol as there are grams moist iodine, and take 1/20 the weight of the latter of red phosphorus. From 2000 grams iodine I obtained 1720 grams distilled ethyl iodide in this manner. Thus it becomes possible to make a limited quantity of iodine furnish a practically unlimited amount of zinc ethyl.

THE USE OF ACETYLENE GAS AS FUEL IN CHEMICAL LABORATORIES.

By Arthur Lachman.

Solons who have located so many of our colleges in small towns, far from the highways of civilization, were probably actuated by the best of motives; but it cannot be denied that they have dealt unkindly with the disciples of science, by depriving them of the use of coal-gas. Bunsen's ingenious introduction of this fuel into our laboratories has wrought such a change in experimental methods that the organization of a modern laboratory without a liberal supply of gas would seem an absolute impossibility. And so there have arisen the numerous substitutes which are designed to supply the place of coal-gas. Of these substitutes, it would seem that "gasoline gas" enjoys the greatest popularity. This "gas" is made by simply saturating air with gasoline vapor. For this purpose a variety of contrivances are on the market, the details of which need not be considered here. It is evident at once that such a gas is open to serious objections, the chief of which is the condensation of gasoline in the pipes whenever the temperature sinks appreciably. Another objection is to be found in the comparatively small proportion of vapor to air in this gas; a sample of saturated gas which

I recently analyzed for another purpose, contained only 23 per cent of gasoline vapor; and in a certain form of machine in common use, the proportion is lowered to 15 per cent, to obviate the condensation above referred to. As a result of this rather attenuated condition of the combustible vapor, it has an unfortunate tendency to blow out at the burners unless both the rate of flow and the pressure are carefully regulated to the construction of the burner.

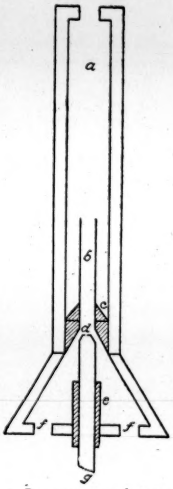
Our laboratory is supplied with such a tantalizing fuel. In drawing up the plans for a new laboratory building, however, it was found that our machine must be either enlarged or replaced; and the opportunity was seized to ascertain whether or not acetylene would prove an adequate substitute in point of cost, convenience, and feasibility. I was unable to secure data, either from the current journals or the manufacturers of acetylene burners, relative to other than the mere cost of installation; and it may therefore be of interest to other isolated chemists to record here the results of my investigations. The data which I have collected may be presented under three heads: (1) The acetylene Bunsen burner; (2) the properties of the acetylene blue flame; (3) the comparative operating expenses of acetylene and gasoline gas.

1. The Acetylene Bunsen Burner.

The burners employed in my experiments were kindly supplied by Mr. Breck, Pacific Coast agent of Messrs. Colt & Co., of New York. They are ingeniously constructed of heavy brass, and have certainly solved the problem of furnishing an acetylene flame which does not deposit soot. The essential details of construction are given in the following sketch, which shows the actual dimensions.

The pin-hole supplying gas is very small, and no variations of its orifice are possible; so that it is quite likely that exposure to laboratory fumes will interfere somewhat with its operation. The burner is supposed to work under a pressure of six inches of water, and at this pressure yields a flame about 4½ inches high and ⅝ inch in diameter. However, it begins to furnish a fairly good flame at a pressure of three inches; below this the flame becomes luminous.

The burner suffers from a number of defects, which are probably due more to the nature of acetylene than to errors in construction. In the first place, the flame cannot be lowered successfully; the operation requires a very delicate adjustment of the hose-cock, and at best the flame is shortened not more than one inch before it becomes luminous or strikes back. This striking back is the second objection to the burner; for it invariably occurs whenever the gas is turned off. In itself, this would probably not prove objectionable; but it is accompanied by a loud report like the crack of a rifle. It is plain that such a burner would furnish considerable diversion to the average student, and play havoc with the nerves of his instructor. Incidentally, this forcible striking back forms an interesting lecture demonstration of the explosive violence of acetylene-air mixtures; for the total volume of the burner tube is not more than 5 cc.



a. Burner tube: *b*. Inner mixing tube; *c*. Cone valve for regulating air supply; *d*. Pin-hole for admitting acetylene; *e*. Screw collar for air valve; *f*. (Four) air-holes; *g*. Acetylene entrance.

2. *The Properties of the Acetylene Blue Flame.*

It is a trifle incorrect to speak of the acetylene *blue* flame, for the gas burns with a purple color resembling the potassium flame. It cannot therefore be used for flame tests; the color is not absorbed by cobalt glass. Spectroscopic examination revealed the interesting fact that the phenomenon is due to a continuous spectrum, in which red is poorly developed and yellow almost entirely lacking. No lines were observable with my small instrument, even the sodium line being completely absent. The central cone of the acetylene flame is exceedingly small, being not more than 3/16 inch high; it has the regular blue-flame appearance, and is very hot (*cf.* below).

Very beautiful effects are obtained if the air-supply is slowly cut off. At first a faint yellow central cone makes its appearance, which then becomes brilliantly white; while at the same time the outer and upper portions of the flame assume a deeper purple tint. Further diminution of air causes a second central cone to envelop the first; it is less lustrous than the latter, and stands out sharply. By very careful manipulation as many as four such cones can be formed within the same flame; and finally the whole jet becomes luminous throughout. The phenomena are well suited to illustrate the theory of combustion within the Bunsen burner.

The acetylene Bunsen flame deposits no trace of soot. However, when it is allowed to play against cooled glass surfaces, a not inconsiderable quantity of colorless oil can be collected. This oil is orthophosphoric acid, shown by its reactions with silver nitrate and with cold molybdate. For use in analytical work, the acetylene must needs be carefully freed from phosphine.

In spite of the high phosphorus content, the burning gas had no determinable effect upon platinum. A piece of very thin foil weighing 0.7 gram was loosely coiled and heated to white heat for over an hour; it had not gained even 1/50 milligram. The same piece was then hung so that its lower edge was bathed by the blue central cone; further heating for an hour and a half did not alter its weight. The phosphine of commercial acetylene would thus seem to have no appreciable action on platinum. The portion of foil which had been hung in the blue flame was etched as if eaten by acid; and at one point two edges had fused together for over ¼ inch. This would indicate a very high temperature in the flame. An additional indication may be found in the much greater luminous intensity of the platinum.

Very intense effects are obtained in the acetylene blast. Using an ordinary Bunsen blast-lamp with foot-bellows, No. 27 platinum wire (diam. 0.33 mm.) melted as easily as in oxyhydrogen. Platinum foil was turned on its edge. In an attempt to use an oxygen-acetylene blast, the blowpipe itself burned away so quickly that the experiment could not be continued. In both cases the flame was white, not colorless.

In spite of the high temperature of the acetylene flame, however, its heating capacity is very small compared with gasoline gas. This is well shown by the following test: A Jena one-liter flask was employed, containing exactly 500 cc. water. The flames were adjusted to play directly against the glass, the distance from burner tip to flask being one-third the height of the full flame. The time was noted from lighting the burner until the water came to boiling:

Acetylene burner No. 1	13 min.
Acetylene burner No. 2	10 "
" Detroit " burner	4½ "

The gasoline burner was an ordinary laboratory specimen, rather below than above the average. It remains to be said in this connection that gasoline and acetylene burners have widely different gas capacities, and that herein lies a partial explanation of this great difference in heating power. This topic will be discussed again below.

3. The Comparative Cost of Acetylene and Gasoline Gas.

The rate of consumption was measured by noting the fall of a gasometer tank of known capacity. In these tests the above acetylene burners were used, as well as two Detroit burners; the acetylene burners were worked at a pressure of 6 water-inches, the others at the pressure of our gas-machine (1¼ inches).

Burner.	I.	II.	III.	IV.
Consumption per hour in cubic feet.	0.83 0.80	1.0 1.0	5.9	4.3

These figures come very near those claimed by the manufacturers; *viz.*, 1 and 5 feet, respectively.

Carbide is quoted here at about $6.00 per hundred pounds; gasoline costs about 25 cents per gallon laid down. One hundred pounds of carbide furnish an average yield of 500 feet of acetylene; one gallon 86° gasoline produces about 200 feet of "gas." Per cubic foot acetylene costs 1.20 cents, gasoline gas .0125 cents. Per burner hour the cost becomes: acetylene 1.20 cents, gasoline .0625 cents.

To obtain an adequate idea of the cost of supplying each student with gas during the year, no accurate data are at

hand; and for my purposes I have assumed that the average student, either elementary or advanced, may be fairly supposed to keep one burner in continual operation each hour he spends in the laboratory. This seems a fair allowance for waste, extravagance, the possession of several burners, and the employment of gas for general purposes (lectures, air-baths, etc.). This assumption has checked with the cost of supplying this laboratory. With an average of thirty-five weeks spent in laboratory work each year, the student will consume for each hour per week in gasoline 22 cents, in acetylene 42 cents. These figures are excessive, owing to the unreasonably high tariffs on the Pacific Coast; but in all probability the cost of materials is proportionately lower elsewhere. It should be noted, however, that in actual operation acetylene will be at a disadvantage owing to its smaller heating capacity, so that work such as maintaining air-baths at high temperatures, prolonged evaporations, etc., will call for greater expenditure of gas than allowed for here.

4. Conclusions.

In answer to the question: "Will it pay a laboratory to use acetylene in place of gasoline gas," I think that the foregoing results point to the negative. In many ways, this is to be regretted, as a concentrated, non-condensible gas possesses great advantages over the article in present use. A number of points remain for discussion. The first refers to cost of installation. At first sight, acetylene appears to have the advantage. For equal burner capacity, an acetylene plant is considerably cheaper than a properly equipped gasoline generator. As the gas pipes need have only one-fifth the carrying capacity otherwise called for, a very appreciable saving is effected here also. Against this, however, there is to be set the fact that a purifier which will remove phosphine is absolutely essential. There are no data upon which to base computations of the cost of this operation, but it cannot be very cheap either in installation or in maintenance. Again, even a very large acetylene generator must be cleaned out at least every two weeks, whereas the other machine can run six months without attention. The cost of burners for

either system is about the same; but a laboratory already well supplied with ordinary burners must purchase a completely new outfit.

Secondly, the difficulties of adjusting the flame of acetylene to small size would preclude its use in all delicate work, such as fractional distillation, thermostat regulation, melting-point determinations, etc. It certainly does not seem practical to have *two* kinds of gas in a laboratory. The use of a small, luminous acetylene jet is out of the question, on account of the inevitable heavy deposit of soot.

The small heat capacity of acetylene, which at first sight seems surprising, is readily explained upon thermochemical data. The comparison must be made between one volume of acetylene and five volumes of "gasoline gas." The latter contains about 20 per cent of vapor, and the vapor, according to some rough experiments I have made, seems to have an average composition of C_5H_8; so that we are really comparing equal volumes of acetylene and propane. The heat of combustion of the former is about 3100 K, of the latter 5500 K. The remaining balance in favor of gasoline gas is probably due to the greater surface of contact which its flame presents to the heated objects.

It would thus seem that neither in cost, convenience, nor feasibility can acetylene compete with gasoline as a laboratory fuel. Nor does the future seem likely to bring any adequate change in this matter. Any decrease in the cost of carbide can surely be met by the oil people; nor are the defects of acetylene as a fuel such as can be remedied by improved burner construction.

EUGENE, OREGON, March, 1900.

THE REACTIONS OF ANILINE AND HYDROXYLAMINE WITH HYDROXY- AND UNSATURATED COMPOUNDS.

BY ALFRED TINGLE.

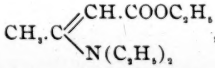
THEORETICAL.

The work of W. Wislicenus[1] and of N. R. Schiff[2] has shown that many so-called β-ketonic esters are in reality mixtures of

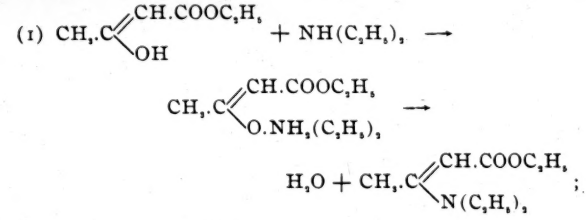
[1] Ann. Chem. (Liebig). **291**, 147–216; Ber. d. chem. Ges., **32**, 2837–2840.
[2] *Ibid.*, **31**, 205–209; 601–609.

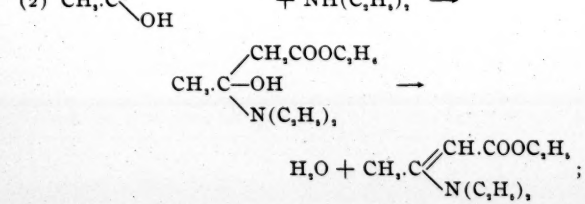
two substances, one containing the group —CO.CH_2.COOR, the other the tautomeric form —C(OH) : CH.COOR. Whilst these bodies are readily interconvertible, by the action of solvents for example, nevertheless each has, it would seem, a real existence.

Hitherto no attempt appears to have been made to answer the question as to which of the reactions, long recognized as characteristic of the class, are peculiar to the enolic, which to the ketonic form, and which may be considered common to both. For example, Kuckert[1] showed that ethylic acetoacetate and diethylamine give the compound



and believed that it was necessarily produced from the enolic form. It is now seen to be probable that an intermediate compound is formed, and the reaction might take one of the three courses represented below :





[1] Ber. d. chem. Ges., 18, 619.

(3) $CH_3.C(=O).CH_2.COOC_2H_5 + NH(C_6H_5)_2 \longrightarrow$

$CH_3-C(CH_2.COOC_2H_5)(OH)-N(C_6H_5)_2 \longrightarrow$

$H_2O + CH_3.C(=CH.COOC_2H_5)-N(C_6H_5)_2$.

It is, of course, also possible that any two, or all, of these reactions might occur together. The hypothetical intermediate products in cases (2) and (3) are identical, so that neither their isolation nor an indisputable proof of the constitution of the final compound, would, in reality, throw any light on the structure of the original reacting molecule. In fact, a casual observer might be misled. Freer[1] has shown that acetone-*p*-bromphenylhydrazone, probably possesses the formula

$$CH_3>C(CH_3).NH.NH.C_6H_4Br,$$

yet it can by no means be concluded that $CH_3>C(CH_3).OH$ would be a correct representation of acetone.

It is, on the other hand, possible that a true unsaturated alcohol group should appear to act like a ketone, somewhat in the following manner:

$$R-CH=C(OH)-R + NH_2R \longrightarrow R-CH_2-C(OH)-NHR \longrightarrow R-CH_2-C=NR$$

The work described in this paper was undertaken in the hope of throwing some light on the question as to what reactions can properly be described as taking place, either wholly or in part, through the activity of the group —CH=C(OH). It appeared that this end might be, to some extent, attained

[1] This JOURNAL, 21, 16.

by examining the reactions of bodies which, whilst containing no double carbon linkage, possess a hydroxyl group, and also one or more highly negative radicals that might render the hydroxyl more active. The reaction (1) above does not depend directly on the double linkage of carbon, and should it really represent the course of events, analogous cases might be encountered. It was also decided to study bodies containing a highly negative group and a double carbon bond, but no hydroxyl. Should addition-products, analogous to the hypothetical intermediate substance in (2), be obtained under these circumstances in any given reaction, we should be justified in believing that the enolic form takes a direct, though perhaps not the whole, part in the corresponding reaction of a ketonic acid. As an example of the first class, ethylic tartrate was selected for preliminary study, while the second class is represented by ethylic cinnamate.

Phenols have also been examined to some extent, but here the case is more uncertain, according to the acceptance or non-acceptance of the Kekulé formula for them. In view, however, of the resemblance pointed out originally by Geuther[1] between ethylic acetoacetate and esters of salicylic acid, it seemed desirable further to investigate the latter with a view of more strict comparison.

Though the results obtained do not, as yet, warrant any decisive conclusion, it is desired to place them on record, whilst the work is continued and extended.

Arppe[2] has shown that when tartaric acid and aniline are heated together at 150° a mixture of tartranilide and tartranil is produced.

In the present investigation ethylic tartrate was employed, and the reaction took a different course. When these substances were brought together under pressure at 100°, in aqueous alcoholic solution, no action could be observed, but on boiling the ester with aniline for somewhat longer than an hour, a mixture was obtained which was extracted with boiling water. Tartranilide, which melts and decomposes at 255°–256°, remained undissolved. On evaporating the aque-

[1] Ann. Chem. (Liebig), **244**, 190–221.
[2] *Ibid.*, **93**, 352–357.

ous extract, a body was deposited which crystallizes in plates and melts, without decomposing, at 151°–152°. It has the composition $C_{11}H_{13}NO_4$ and appears to be ethylic phenyltartramate, $\begin{matrix}CHOH.COOC_2H_5\\ |\\ CHOH.CO.NH.C_6H_5\end{matrix}$. It is readily soluble in a cold solution of potassium hydroxide, but less readily so in a solution of sodium carbonate, even when warmed. Grote[1] and Demondesir[2] have shown that tartaric ester reacts in a somewhat similar manner with ammonia. We thus see that, in what may be considered a typical instance, hydroxyl, closely associated with carbonyl groups, but attached to a saturated carbon atom, is inactive towards amines, and not capable of forming either the group $R.NH.\overset{\diagdown\diagup}{C}.CO$, or the intermediate compound $R\ NH_2.\overset{\diagdown\diagup}{C}.CO$.

Several attempts were made to bring about a reaction between ethylic tartrate and hydroxylamine. They were uniformly unsuccessful, and it appears almost certain from these that the reaction

$$HO.\overset{\diagdown\diagup}{C}.COOR + NH_2OH = HO.NH.\overset{\diagdown\diagup}{C}.COOR + H_2O$$

will not take place except in the presence of a double carbon bond. Obviously, however, it would not be safe to consider this conclusion final till many more cases have been investigated.

Some preliminary observations were next made upon the reactions of aniline and hydroxylamine with an unsaturated ester. For this purpose ethylic cinnamate was chosen.

It is conveniently obtained by use of the modification of Fischer's method[3] proposed by J. Bishop Tingle and the writer.[4] The yield is excellent.

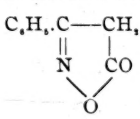
On heating ethylic cinnamate with aniline in aqueous-alcoholic solution to 100°, under pressure, for four hours, no combination took place. Here we see that aniline is apparently

[1] Ann. Chem. (Liebig), **130**, 203.
[2] *Ibid.*, **80**, 303.
[3] Ber. d. chem. Ges., **28**, 3152.
[4] This JOURNAL, **21**, 243.

incapable of adding itself at a double carbon bond. It is, however, possible that with a more basic amine, or an acid containing a greater number of negative groups, a reaction might occur.

Led by its analogy to sodium camphoroxalate (which readily reacts with amines[1]) an experiment similar to the above was tried, sodium cinnamate being substituted for the ester. No action could, however, be detected.

Thiele and Pickard[2] have examined the action of hydroxylamine on ethylic cinnamate in the presence of sodium ethoxide, and obtained cinnamhydroxamic acid (m. p. 111°.5). The writer's experiments were conducted under very different conditions. Hydroxylamine was liberated from the hydrochloride by an aqueous solution of sodium carbonate, and only enough alcohol was added to bring the ethylic cinnamate into solution. After standing from one to three days, two bodies were found to be produced. The first is an oil, the investigation of which is still incomplete. The second compound crystallizes from dilute alcohol in yellow needles ; it is soluble in warm alkalies, and its alcoholic solution gives, with ferric chloride, a brownish color. It melts and evolves gas at 144°.5, and appears to be identical with phenylisoxazolone,



previously obtained by Claisen and Zedel[3] from ethylic benzoylacetate and hydroxylamine. The production of this compound involves a partial oxidation at some point in the reaction, and the exact mechanism cannot be understood till the accompanying product has been more fully investigated ; it is clear, however, that the addition of hydroxylamine to the double bond is an essential feature. Such an addition has already been observed in the case of sodium camphoroxalate by J. Bishop Tingle,[4] and of phorone by C. Harries and F. Lehmann.[5]

[1] This JOURNAL, **21**, 239 ; **23**, 214-230. [2] Ann. Chem. (Liebig), **309**, 189-205.
[3] Ber. d. chem. Ges., **24**, 140. [4] This JOURNAL, **19**, 396.
[5] Ber. d. chem. Ges., **30**, 231, 2726.

The oil previously mentioned boiled under reduced pressure at the same temperature as cinnamic ester, but a solid separated from the distillate which melted at 93° and was readily soluble in cold water. Potassium hydroxide, even at the ordinary temperature, hydrolyzes the oil to cinnamic acid. On treatment with an alcoholic solution of hydroxylamine at the temperature of the laboratory, it gave phenylisoxazole, and a body which melts at 65°–67° and is readily soluble in alcohol and chloroform, crystallizing therefrom in plates. When allowed to stand for several days with ethylic acetate, the oil deposited a white solid which melts and decomposes at 216°–217°.

It was not found possible to bring about any reaction between potassium cinnamate and hydroxylamine.

The interaction of hydroxylamine and ethylic cinnamate, and its non-occurrence when ethylic tartrate replaces the latter, points directly to the activity of the enolic, as well as of the ketonic, form of "ketonic" acids when in contact with hydroxylamine, and also shows that this activity is primarily due to the presence of a double carbon bond, and not to the influence of the hydroxyl group.

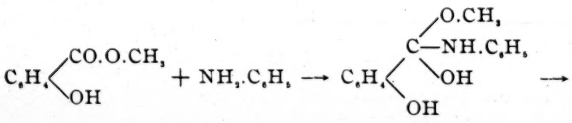
Geuther[1] insisted on the analogy between the behavior of acetoacetic and salicylic esters, but his argument was chiefly based on the similarity of reaction with potassium hydroxide and carbon dioxide, potassium cyanide, and ferric chloride. There seems to be little analogy in their reactions with hydroxylamine.

Hantzsch[2] showed that when hydroxylamine and ethylic acetoacetate were mixed in alkaline solution, the chief product was methylisoxazolone, $CH_3.C\begin{matrix}=N-O\\ \quad\quad |\\ -CH_2-CO\end{matrix}$, although in presence of ammonia an unstable compound was formed, which he supposed to be acetoacetylhydroxamic acid,

$$CH_3.CO.CH_2.C\begin{matrix}=N.OH\\ \quad\quad\quad\

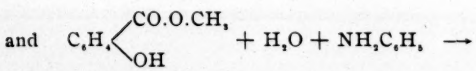
Prior to this, Jeanrenaud[1] stated that methylic salicylate and hydroxylamine give, in alkaline solution, salicylhydroxamic acid. As a doubt of the accuracy of this work has been for some reason expressed by H. Meyer,[2] and as the point seemed to be one of interest, Jeanrenaud's work was repeated. It was found that when methylic salicylate, hydroxylamine hydrochloride and a slight excess of potassium hydroxide were mixed in aqueous alcoholic solution, salicylhydroxamic acid was produced. Its properties were those ascribed to it by Jeanrenaud. No reaction was found to take place between sodium salicylate and hydroxylamine.

Limpricht[3] has studied the action of aniline upon the monohydroxylbenzoic acids at high temperatures. He found that salicylic acid gave, under these conditions, a small amount of salicylanilide and much phenol. The writer finds that when aniline is boiled with methylic salicylate, both substances being carefully dried before use, the sole products are phenol and methylaniline. When the ordinary amount of hydroscopic moisture was not removed a very small quantity of salicylanilide was formed, but the yield clearly indicated that it was a secondary reaction induced by the presence of water. Methylaniline was identified, as usual, by the formation of methylacetanilide; the yield was very good and it is hoped to extend this reaction to the production of other alkylanilines. The mechanism of the reactions may be represented as follows:



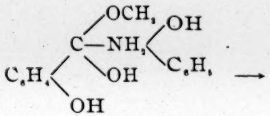
$$C_6H_4\begin{cases}CO.O.CH_3\\OH\end{cases} + NH_2.C_6H_5 \longrightarrow C_6H_4\begin{cases}C(O.CH_3)(NH.C_6H_5)\\OH\end{cases} \longrightarrow$$

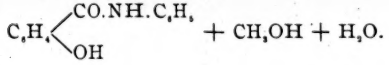
$$C_6H_4OH + CO_2 + CH_3.NH.C_6H_5;$$



$$\text{and} \quad C_6H_4\begin{cases}CO.O.CH_3\\OH\end{cases} + H_2O + NH_2C_6H_5 \longrightarrow$$

[1] Ber. d. chem. Ges., **22**, 1273.
[2] "Determination of Radicles in Carbon Compounds," American Edition, p. 74.
[3] Ber. d. chem. Ges., **22**, 2907.





Aniline, when boiled with orthonitrophenol for four hours, gives a compound resembling azophenine in its solubilities, appearance, and behavior with concentrated sulphuric acid. It melts sharply, however, at 201°, while the melting-point of azophenine is given as 241°. No analysis has yet been made, as the yield is poor. When paranitrophenol is substituted for the ortho-compound a black amorphous powder is the sole product.

EXPERIMENTAL.

Ethylic Tartrate and Aniline.

These bodies react to produce two compounds, tartranilide, which has already been prepared by Arppe,[1] and a substance which melts, when pure, at 151°–152°. Ethylic tartrate, 5.1 grams (1 mol.), and aniline, 13.9 grams (6 mols.), were boiled together for two hours. The product was then distilled in steam. When the excess of amine had been removed in this manner, the residue in the flask was quickly filtered, tartranilide remaining undissolved in the hot water.

The tartranilide so obtained is pure after a single crystallization from hot alcohol. It was found to melt and decompose at 255°–256°. Arppe merely gives the temperature as "above 250°." Its properties are identical with those ascribed to it by him; it was further identified by analysis:

Substance taken, 0.3111 gram; CO_2 formed, 0.7284 gram; H_2O formed, 0.1562 gram.

	Calculated for $C_{18}H_{18}N_2O_4$.	Found.
C	64.00	63.85
H	5.33	5.58

[1] Ann. Chem. (Liebig). **93**, 352–357.

The substance which was soluble in hot water was purified by crystallization, first, from dilute alcohol, and finally from water. It was deposited in small white plates and melted, when pure, at 151°–152°.

The analytical results indicate that it is ethylic phenyltartramate, $\begin{matrix} CH(OH)—CO.NH.C_6H_5 \\ | \\ CH(OH).COOC_2H_5 \end{matrix}$.

Analysis:

0.2011 gram substance gave 10.7 cc. moist nitrogen at 25° and 749 mm.

Substance taken, 0.2084 gram; CO_2 formed, 0.4378 gram; H_2O formed, 0.1150 gram.

	Calculated for $C_{12}H_{15}NO_5$.	Found.
C	56.91	57.29
H	5.92	6.13
N	5.53	5.92

The compound readily dissolves in a cold solution of potassium hydroxide. It does not dissolve in a cold solution of sodium carbonate, but does so slowly on warming.

Ethylic Tartrate and Hydroxylamine.

Attempts were made to bring about a reaction between these bodies. Ethylic tartrate was mixed with varying proportions of hydroxylamine hydrochloride in the presence of sodium ethoxide, sodium carbonate, or sodium acetate, and also with an alcoholic solution of free hydroxylamine. In no case was any reaction found to occur.

Preparation of Ethylic Cinnamate.

E. Fischer's method of esterification, modified according to the suggestion of J. Bishop Tingle and the writer,[1] was employed, and was found to act admirably; 15 grams of cinnamic acid, boiled for three and a half hours with 100 cc. of 90 per cent alcohol and 7 cc. of concentrated sulphuric acid, gave 15.8 grams of ester, or 91.8 per cent of the theoretical. A comparison was made with the result obtained when using absolute alcohol (2.5 cc. concentrated sulphuric acid to 100 cc. alcohol);

[1] This JOURNAL, **21**, 243.

it was found that the yield of ester was 98.8 per cent. When working with considerable quantities, however, the loss of ester is unimportant in comparison to the saving in the cost of the alcohol.

Ethylic Cinnamate and Aniline.

An attempt was made to obtain an addition-product from equimolecular proportions of ethylic cinnamate and aniline, by heating them at 100° during four hours, under pressure, in the presence of alcohol. No combination, however, occurred. A similarly negative result was obtained when sodium cinnamate was substituted for the ester.

Ethylic Cinnamate and Hydroxylamine.

When these substances react upon each other in dilute alcoholic solution, two bodies are formed, the first of which is an uncrystallizable oil which has not yet been thoroughly investigated. The second, a crystalline compound, appears to be identical with Claisen and Zedel's phenylisoxazole.[1] It melts and decomposes at 144°.5.

Hydroxylamine hydrochloride, 20.4 grams (3 mols.), and sodium carbonate, 16.8 grams (1.5 mols.), were mixed in aqueous solution, and ethylic cinnamate, 17.2 grams (1 mol.) added, with sufficient alcohol to dissolve it entirely. The whole was allowed to stand three or more days at the temperature of the laboratory. At the end of that time the greater part of the alcohol was boiled off, water was added, and the oil which separated was extracted with ether. The aqueous layer was next slightly acidified with dilute sulphuric acid, filtered, and again extracted with ether. The substance precipitated was identical with that subsequently obtained on evaporating the ether, the total yield of crude product being 4.5 grams. It was purified by draining on a porous tile and subsequently crystallizing from dilute alcohol.

Analysis:

Substance taken, 0.2490 gram; CO_2 formed, 0.6140 gram; H_2O formed, 0.1148 gram.

0.1487 gram substance gave 11.5 cc. N at 22° and 740 mm.

[1] Ber. d. chem. Ges., **24**, 140.

	Calculated for $C_9H_7NO_3$.	Found.
C	67.08	67.25
H	4.34	5.12
N	8.69	8.52

Determination of molecular weight.[1]

Value of K for solvent (phenol) = 75.00.

Amount of substance taken. Gram.	Δ.	Molecular weight.
0.1260	0°.33	143.7
0.2510	0°.70	134.9

Amount of solvent employed, 19.9320 grams.

The compound crystallizes in golden-yellow needles, as described by Claisen and Zedel,[2] who give its melting-point as 147°. Its alcoholic solution gives a brownish coloration with ferric chloride.

Potassium Cinnamate and Hydroxylamine.

Attempts were made to bring about a reaction between these compounds, in the presence of potassium hydroxide, sodium carbonate, or sodium acetate, both by prolonged action at the temperature of the laboratory and by heating on the water-bath. No success was attained.

Methylic Salicylate and Hydroxylamine.

The reaction between these substances has already been investigated by Jeanrenaud,[3] but some doubt having been thrown on the results obtained by him, it was considered advisable to reinvestigate the matter. The experimental conditions were slightly changed before obtaining the best results, but the formation of salicylhydroxamic acid was fully confirmed.

Hydroxylamine hydrochloride, 6.9 grams (2 mols.), was mixed, in aqueous solution, with 14 grams (5 mols.) of potassium hydroxide; 7.6 grams (1 mol.) of methylic salicylate were added, with sufficient alcohol to bring the whole into solution. The mixture was allowed to stand at the temperature of the laboratory for two days. A slight excess of dilute

[1] I am indebted for this determination to Mr. R. D. Hall, of this university.

[2] *Loc. cit.*

[3] Ber. d. chem. Ges., **22**, 1270–1284.

sulphuric acid was next added, the acid liquid was diluted with water and extracted with ether. The extract, after distilling off the ether, was steamed on the water-bath to remove traces of salicylic acid. In this way a residue of salicylhydroxamic acid was obtained. It was recrystallized from alcohol, and, after purification, melted and decomposed at 171°.

Analysis:

Substance taken, 0.2367 gram; CO_2 formed, 0.4727 gram; H_2O formed, 0.1001 gram.

	Calculated for $C_7H_7NO_3$.	Found.
C	54.90	54.46
H	4.57	4.69

That a slight departure from the conditions described causes a great difference in the course of the reaction is shown by the following experiment:

The methylic salicylate and hydroxylamine hydrochloride were mixed in the same proportions as before, but only three molecular proportions of sodium hydroxide were added, and a quantity of alcohol insufficient to completely dissolve the ester. The reaction was allowed to continue for sixty-six hours. The only product obtained was salicylic acid. It is possibly through the occurrence of some such variation that doubt has been cast on Jeanrenaud's accuracy.

Sodium Salicylate and Hydroxylamine.

Attempts to obtain, from sodium salicylate and hydroxylamine, an addition-product, similar to that obtained by J. Bishop Tingle[1] from sodium camphoroxalate and hydroxylamine, were unsuccessful. Salicylic acid was invariably regenerated.

Methylic Salicylate and Aniline.

The nature of the reaction in this case varies, according to whether hygroscopic moisture is or is not excluded. When the dried substances are boiled together in a carefully dried apparatus the products of the reaction are phenol and methylaniline. The details of the experiment are as follows:

[1] This JOURNAL, **19**, 396.

Methylic salicylate, 15.2 grams (1 mol.) dried by means of calcium chloride, was boiled for five hours, in a well-dried reflux apparatus, with 45.5 grams (5 mols.) of aniline dried over sodium. The resulting oil was distilled, leaving only a small quantity of an uncrystallizable tar in the distilling flask. The distillate was shaken with a solution of potassium hydroxide and then extracted with ether. The material soluble in ether boiled between 180° and 186°, and consisted of a mixture of aniline and methylaniline. These were separated by conversion into their sulphates, that of methylaniline being readily soluble in water. Free methylaniline was subsequently recovered, and was recognized by the formation of methylacetanilide (melting at 101°–103°) on treatment with acetyl chloride. The yield of methylaniline by this reaction is good. The alkaline aqueous solution, after the removal of the bases, was acidified with dilute sulphuric acid ; oily drops separated; they were identified as phenol by their smell and by the formation of tribromphenol, melting at 91°–92°.

A series of experiments was also conducted in a similar manner, but without taking any precautions in drying the materials used. Under these circumstances it was found that in addition to methylaniline and phenol, salicylanilide was always formed. This remained behind after distilling off the phenol and mixture of bases. It was drained on tile and it then crystallized from dilute alcohol in warty tufts of needles, melting at 132°. Analysis :

Amount of substance taken, 0.2926 gram ; CO_2 formed, 0.7825 gram ; H_2O formed, 0.1370 gram.

	Calculated for $C_{13}H_{11}O_2N$.	Found.
C	73.23	72.93
H	5.16	5.20

That the formation of salicylanilide is the result only of a secondary reaction is shown by the smallness of the yield. In one experiment 15.2 grams of methylic salicylate and 46.5 grams of aniline were employed : only 0.8 gram of crude salicylanilide was obtained, whilst at the same time 7.4 grams of phenol, and 28.5 grams of the mixed bases were isolated.

Various experiments were made to induce aniline to react

with methylic salicylate at 100°, in analogy with the formation of β-anilidocrotonic ester,[1] but these were unsuccessful.

An attempt to cause aniline and sodium salicylate to react in a manner similar to that leading to the formation of phenylcamphoformeneaminecarboxylic acid from camphoroxalic acid[2] and aniline, was also not successful.

Orthonitrophenol and Aniline.

o-Nitrophenol, 10 grams (1 mol.), was boiled for four hours with 28 grams (4 mols.) of aniline. The resulting mixture was made alkaline and distilled in steam, then made acid, and again distilled in steam. The contents of the distilling-flask were filtered. The insoluble substance thus separated was purified by boiling with alcohol to remove the tar, and crystallized from chloroform. So purified it forms plates having a red-brown color. It melts quite sharply at 200°–201°. With concentrated sulphuric acid it gives a reddish color when cold, but a clear blue one when strongly heated. It is probably formed by an oxidation-product of the aniline condensing with other aniline molecules. When the heating of aniline and *o*-nitrophenol is long continued only a black uncrystallizable powder is produced.

Paranitrophenol and Aniline.

These bodies, when boiled together for six hours, yield only a black amorphous powder; there is evidently a difference of a pronounced kind between the actions of these nitrophenols with aniline.

It is hoped in the future to continue and extend this work in various directions.

CHEMICAL LABORATORY, UNIVERSITY OF WISCONSIN.

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[1] Ber. d. chem. Ges., **20**, 944.

[2] This JOURNAL, **21**, 239; **23**, 225.

Contributions from the Sheffield Laboratory of Yale University.

LXXV.—ON THE MOLECULAR REARRANGEMENT OF THE THIONCARBAMIC, THIONCARBANILIC, AND THIONCARBAZINIC ESTERS: β-ALKYL-α-μ-DIKETOTETRAHYDROTHIAZOLES.

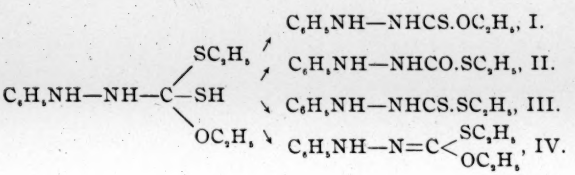
By Henry L. Wheeler and Bayard Barnes.

In a recent paper we showed that the thioncarbamic esters, $H_2NCS.OR$, undergo a molecular rearrangement in the presence of alkyl halides, with great ease, giving the isomeric thiol compounds, $H_2NCO.SR$. In this paper we describe the results of an examination of certain monosubstituted xanthogenamides, $XNHCS.OR$, under similar conditions and of the preparation of some homologues of "mustard-oil acetic acid" or α-μ-diketotetrahydrothiazole.

We find, when X in the above formula is C_6H_5—, that these compounds, the thioncarbanilic esters, react less readily than the non-substituted thioncarbamic esters. With methyl and ethyl iodides they require more or less protracted heating, while with isobutyl iodide no rearrangement was observed. In order to extend our knowledge of the thion esters, we examined also the phenylthioncarbazinic esters, C_6H_5NH—$NHCS.OR$, in which X is the positive grouping C_6H_5NH.

Of the three possible types of phenylthiocarbazinic esters certain dithio[1] and thiol[2] compounds have been described, but methods were lacking for the preparation of the thion derivatives. It seemed probable that these compounds would result by the action of phenylhydrazine on the dithiocarbonic esters, although the reaction, if taking place between equal molecules and if confined to the β-amino group, and excluding tautomeric forms, might still proceed in four different ways, the dithio ester and the phenylhydrazine first combining to form an addition-product, then decomposing as follows; *i. e.*, with the evolution of mercaptan (I. or II.), or alcohol (III.), or hydrogen sulphide (IV.):

[1] Busch: Ber. d. chem. Ges., **28**, 2635.
[2] Busch and Stern: J. prakt. Chem., **60**, 242.

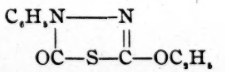


In fact, it was found that this reaction proceeds chiefly in the sense of the first and last representations, a solid and an oil being obtained. The solid material is the phenylthioncarbazinic ester (I.). This reacts readily with methyl iodide, ethyl iodide, benzyl chloride, etc., giving the phenylthiolcarbazinic esters just described by Busch and Stern :[1]

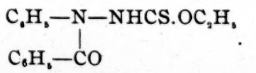
$$C_6H_5NH—NHCS.OC_2H_5 + IR = C_6H_5NH—NHCO.SR + C_2H_5I.$$

This molecular rearrangement takes place at ordinary temperatures, and, therefore, more readily than in the case of the thioncarbanilic esters, a basic character of the molecules being more favorable for rearrangement than a negative one.

Phenylthioncarbazinicethyl ester (I.), reacts with phosgene in toluene, giving ethoxyphenylthiobiazolone (V.), a representative of a new type of alkyloxythiobiazolones, the other theoretically possible types having been described by Busch. The carbazinic ester reacts with benzoyl chloride, evolving ethyl chloride, but the evolution of this gas is due to a secondary reaction, the chief product obtained being a benzoyl derivative (VI.). The same benzoyl derivative is formed from the sodium salt of the carbazinic ester and benzoyl chloride :



V.

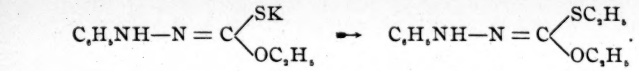


VI.

The formula VI. is assigned to the benzoyl compound because it is soluble in alkali and can be precipitated unaltered by acids. That the benzoyl group is not attached to sulphur is shown by the fact that the compound can be boiled with alkali or acids without decomposition.

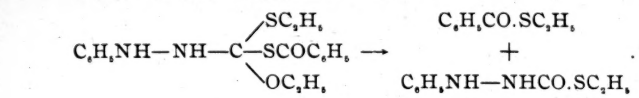
[1] *Loc. cit.*

The action of acyl chlorides is tautomeric when compared with the behavior of the alkali salts of the carbazinic ester with alkyl iodides, for, if phenylthioncarbazinicethyl ester is treated with ethyl iodide in the presence of alcoholic potash the following represents the course of the reaction :



The oil thus obtained being identical in every respect with the hydrazone (IV.), obtained by the direct action of phenylhydrazine on diethyl dithiocarbonate. This behavior is, therefore, similar to that of the thioncarbanilic[1] and the dithiocarbazinic esters,[2] but it differs from that of the oxygen analogues,[3] inasmuch as the latter give nitrogen alkyl derivatives.

When the above hydrazone is treated with thiobenzoic acid a peculiar reaction takes place and phenylthiolcarbazinicethyl ester, (II.), and ethylthiol benzoate are almost quantitatively obtained. The hydrazone and the thio acid combine at the double bond, then separate as follows :



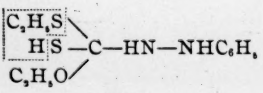
A similar reaction takes place with thioacetic acid. In addition to the above reaction a small amount of hydrogen sulphide is evolved but no acetyl- or benzoylhydrazone was isolated.

The hydrazone can be changed back to the thioncarbazinic ester by passing hydrogen sulphide into the material heated to 125°, or, it can be converted into the thiol ester by treating it with hydrogen chloride in benzene solution. These reactions involve the formation of the following addition-products, which decompose in the two opposite ways, as follows :

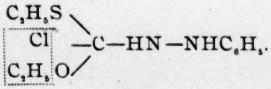
[1] Liebermann : Ann. Chem. (Liebig), **207**, 148; Fromm and Block : Ber. d. chem. Ges., **32**, 2212.

[2] Busch and Lingenbrink : Ber. d. chem. Ges., **32**, 2620.

[3] Hantsch and Mai : *Ibid.*, **28**, 977.



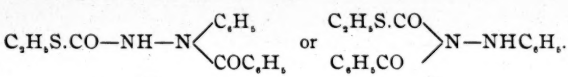
VII.



VIII.

In the case of the action with hydrogen chloride the addition-product (VIII.) was isolated; and in the absence of moisture this is stable at temperatures below 57°.

The hydrazone reacts energetically with acetyl and benzoy chlorides and in the same manner as in the case of the substituted imidoesters, inasmuch as ethyl chloride is evolved and a N-acyl derivative is formed. That the ethyl group attached to oxygen is the one evolved as ethyl chloride in this reaction, and not the group attached to sulphur, is shown by the fact that on boiling the benzoyl derivative with hydrochloric acid phenylthiolcarbazinicethyl ester, (II.), is obtained. The benzoyl compound, therefore, has one of the following thiol structures :



IX. X.

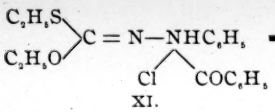
This is confirmed by the fact that the thiol compound,

$$C_6H_5NH—NHCO.SC_2H_5,$$

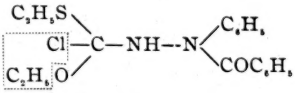
reacts smoothly with benzoyl chloride, hydrogen chloride being evolved, and the above benzoyl derivative is formed. That the structure represented by formula IX. is probably the correct one, or, in other words, that the acyl groups are in the α-β-positions in respect to each other is shown by the acid properties of the compound ; it dissolves in alkalies and can be precipitated, even after boiling, unaltered by acids. Although a diacyl derivative corresponding to the formula X. would be expected to be formed here from analogy with the imido esters. This, however, would probably be insoluble in alkali.

The following, therefore, represents the action of the hydrazone with benzoyl chloride, the addition taking place with the formation of a pentavalent nitrogen product, XI., and not at

the double union as represented in the case of the isoanilides ;[1] this product then rearranges with loss of ethyl chloride, as shown in formula XII.:



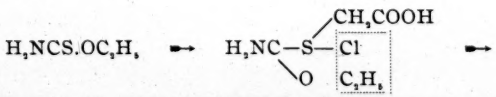
XI.



XII.

The thiocarbazinic esters and the hydrazone are very reactive with compounds of a negative character ; but, on the other hand, with bases they show little tendency to react.

Libermann and Voltzkow,[2] who investigated the action of chloracetic acid on "phenylsulfurethan," and Langlet,[3] who examined the behavior of xanthogenamide with bromacetic acid and β-iodpropionic acid, represented the amides as acting in the pseudoform, and hydrogen chloride as separating in the first stage of the action. It was suggested, however, by P. Meyer[4] that this reaction probably takes place first with the separation of alkyl halide, and this we find to be the case. For example, chloracetic acid reacts with xanthogenamide at 100° in the same manner as with alkyl halides, and there is no reason for assuming, from this reaction, that the thioncarbamic esters have the pseudoform, the reaction taking place as follows :



$H_2NCO.SCH_2COOH.$

XIII.

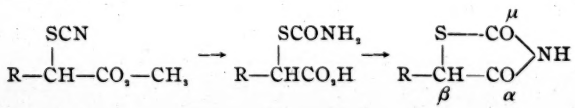
[1] Wheeler and Walden : This JOURNAL, **19**, 130.
[2] Ann. Chem. (Liebig), **207**, 137.
[3] Ber. d. chem. Ges., **24**, 3849.
[4] *Ibid.*, **14**, 1663.

The carbaminthiolglycollic acid, XIII., thus formed, which was isolated, loses water, giving the ring-formed compound, α-μ-diketotetrahydrothiazole (Senfölessigsäure).[1]

XIII. XIV.

Since the acids XCH_2COOH and XCH_2CH_2COOH react readily with xanthogenamide and phenylxanthogenamide, it seemed of interest to determine whether the homologues of the above ring or the β-alkyl derivatives would result in the same manner by employing the halogen acids RCHXCOOH and their esters. It is our experience, however, that these latter compounds react by no means as smoothly as the former; at any rate, a large part of the xanthogenamide undergoes a rearrangement into the corresponding thiol ester and decomposition occurs, giving cyanuric acid, thiol acid, and other products.

We find, however, that the α-sulphocyan derivatives of the fatty acid esters, at least the lower members of the series, are capable of the same transformation under the influence of hydrochloric acid as that observed by Heintz[2] and Claesson[3] in the case of sulphocyanethyl acetate, and that by this means the homologues in question can be prepared. The methyl and ethyl esters give the best yields of the β-alkyl-α-μ-diketotetrahydrothiazoles, the hydrolysis probably taking place as follows:



EXPERIMENTAL PART.

Phenylthioncarbazinicethyl Ester, $C_6H_5NH—NHCS.OC_2H_5$. —115 grams of xanthogenic ester, $C_6H_5SCS.OC_2H_5$, and 80 grams of phenylhydrazine were warmed for twelve hours on

[1] Compare Hantsch and Aripides: Ann. Chem. (Liebig), **249**, 8.
[2] Ann. Chem. (Liebig), **136**, 232.
[3] Ber. d. chem. Ges., **10**, 1352.

the steam bath when hydrogen sulphide and ethyl mercaptan were evolved, and, on cooling, 77 grams of the carbazinic ester separated. This was filtered on the pump and separated from the hydrazone, which latter, after washing with alkali, was dried at 100° in a vacuum, when the oil thus obtained weighed 37 grams.

The carbazinic ester was purified by crystallizing from ligroin or alcohol, from which solvents it separates in the form of needles melting at 72°–74.° A nitrogen determination then gave:

	Calculated for $C_9H_{12}N_2OS$	Found.
N	14.2	14.1

This compound dissolves in alkali and is precipitated unaltered by acids.

Phenythiolcarbazinicmethyl Ester, $C_6H_5NH—NHCO.SCH_3$. —This compound was obtained when two grams of the above ethyl ester were dissolved in 5 grams of methyl iodide. On standing for several hours and then evaporating the methyl iodide, colorless needles melting at 152° were obtained. In spite of the fact that a nitrogen determination came low (analysis A) this material is identical with that prepared from potassium thiolcarbazinate, $C_6H_5NH—NHCO.SK$, and methyl iodide (analysis B) which was first obtained in the latter way by Busch and Stern.[1]

	Calculated for $C_8H_{10}N_2OS$.	Found. A.	B.
N	15.3	14.7	15.5

Phenylthiolcarbazinicethyl Ester, $C_6H_5NH—NHCO.SC_2H_5$, when prepared by treating the thioncarbazinic ester or the salt, $C_6H_5NH—NHCOSK$, with ethyl iodide, was obtained in needles melting at 112.° Busch and Stern give 113.° A nitrogen determination gave:

	Calculated for $C_9H_{12}N_2OS$.	Found.
N	14.2	14.0

This compound is insoluble in alkali. When this and the preceding compound were heated with molecular proportions of aniline, on the steam-bath, carbanilide was obtained.

[1] Loc. cit.

Phenylthiolcarbazinicbenzyl Ester, $C_6H_5NH—NHCO.SCH_2C_6H_5$.—When 3 grams of the thion ester were heated with 1.9 grams of benzyl chloride on the steam-bath, ethyl chloride was evolved and the mixture soon solidified. On crystallizing then from alcohol, clusters of spears or needles were obtained melting at 170°, as stated by Busch and Stern. A nitrogen determination gave:

	Calculated for $C_{15}H_{14}N_2OS$.	Found.
N	10.8	10.0

Ethoxyphenylthiobiazolone, $C_6H_5N—N$ / $OC—S—C—OC_2H_5$.— 5 grams of the thioncarbazinic ester and 13 grams of a 20 per cent solution of phosgene in toluene were heated on the steam-bath for half an hour. On evaporating the solvent in a vacuum, an oil was obtained which finally solidified. The material then crystallized from alcohol in colorless prisms which melted constantly at 38° and a nitrogen determination gave the following result:

	Calculated for $C_{10}H_{10}N_2O_2S$	Found.
N	12.6	12.3

Phenylthioncarbazinicmethyl ester, $C_6H_5NH—NHCS.OCH_3$.—When methylethyl dithiocarbonate, $CH_3OCS.SC_2H_5$, was warmed with phenylhydrazine and then cooled, nothing but an oil was obtained. However, on treating this with ether and alkali, a solid separated which was identical with the above described thiolcarbazinicmethyl ester melting at 152° (analysis C). On adding hydrochloric acid to the alkaline extract and crystallizing the precipitate from alcohol, yellow prisms were obtained melting about 113°. A nitrogen determination gave (analysis D):

	Calculated for $C_8H_{10}N_2OS$.	Found. C.	Found. D.
N	15.3	15.1	15.3

The ether extract contained the hydrazone, $C_6H_5NH—N=C<^{OCH_3}_{SC_2H_5}$, which decomposed when an attempt was made to purify it by distillation under reduced pressure.

α-Benzoylphenylthioncarbazinicethyl Ester, $C_6H_5N(COC_6H_5)NHCS.OC_2H_5$.—When the thioncarbazinic ester is treated with benzoyl chloride, action begins about 90° and is complete on heating to 120° for a short time. On crystallizing from alchol, fine colorless pyramids are obtained melting at 173°. This material is soluble in alkali in which solution it can be boiled without decomposition. A nitrogen determination gave :

	Calculated for $C_{16}H_{16}N_2O_2S$.	Found.
N	9.3	9.3

The sodium salt of thioncarbazinicethyl ester was prepared by mixing the thion derivative with sodium alcoholate and evaporating in a vacuum. It forms a yellowish-red powder. When this was treated with benzoyl chloride the above benzoyl compound was obtained.

Phenylhydrazone of Diethylthiocarbonic Ester, $C_6H_5NH—N=C(OC_2H_5)(SC_2H_5)$.—As stated above, under the heading of phenylthioncarbazinicethyl ester, from 115 grams of xanthogenic ester and the calculated quantity of phenylhydrazine, 37 grams of this hydrazone were obtained. In our first experiments with this substance, it was freed from the thion ester by shaking with alkali, and, after drying, it was distilled under reduced pressure. It was found that it invariably decomposed to some extent when treated in this way, although it boiled for the most part, at 190°–191° at 14 mm. pressure, and at 210°–213° at 36 mm. pressure. Thus obtained, it formed a thick yellowish-red oil which soon became dark-brown and resinous on exposure to the air. A nitrogen determination in a portion which had been distilled indicated that the substance obtained in this manner was not pure (analysis E).

It is better prepared from phenylthioncarbazinicethyl ester by treating the alcoholic solution with potash and ethyl iodide. Action takes place at ordinary temperature and, on filtering and evaporating, washing with water and drying over calcium

chloride, it was found to distil at 198° at 20 mm. pressure. A nitrogen determination gave (analysis F):

	Calculated for $C_{11}H_{14}N_2OS$.	Found. E.	F.
N	12.5	11.5	12.9

The alcoholic solution gives with ferric chloride a garnet-red solution. When hydrogen sulphide was led into this oil at a temperature of 125° for two hours and the material then allowed to cool, a mass of needles or prisms separated. The material was soluble in alkali and, on precipitating with hydrochloric acid and crystallizing from alcohol, fine needles melting at 73° were obtained. This material was, therefore, phenylthioncarbazinicethyl ester.

When hydrogen chloride is led into the hydrazone, dissolved in ether or benzene, a colorless precipitate forms which rapidly deliquesces on exposure. On rapidly pressing it on paper, it was found to melt at about 57° giving off ethyl chloride and leaving a residue of phenylthiolcarbazinicethyl ester.

Phenylhydrazone of Diethylthiocarbonic Ester and Thiobenzoic Acid.—35 grams of the hydrazone were mixed with 20 grams of thiobenzoic acid and warmed on the steam-bath for twelve hours. On cooling, the material partially solidified. It was filtered as far as possible on the pump, and the solid material was crystallized from alcohol when prismatic crystals were obtained, melting constantly at 112.° These proved to be *phenylthiolcarbazinicethyl ester*. The oil filtered from this was distilled at 16 mm. pressure whereupon it boiled mostly at 129°–131.° It was redistilled several times at ordinary pressure (760 mm.), and although it decomposed slightly by this treatment, it boiled constantly at 252°–253°. The boiling point of *ethyl thiolbenzoate*, $C_6H_5CO.SC_2H_5$, is given by Engelhardt, Latschinoff and Malyscheff[1] as 243° and by Seifert[2] as 241°–243.° In order to compare the above oil with ethyl thiolbenzoate, thiobenzoic acid, freshly prepared, was treated with alkali and ethyl bromide in alcohol, when action took place, on warming, and was complete in a few minutes.

[1] Ztschr. Chem., 1868, 356.

[2] J. prakt Chem. (2), 31, 471.

Water was then added and the oil taken up in ether, dried and distilled, when it practically all boiled over from 252° to 253°. On mixing this oil with the above, the boiling-point of the mixture was unaltered. The material was therefore ethyl thiolbenzoate, and the previous observations on the boiling-point of this ester are 10° too low, our observations being taken with an Anschütz thermometer.

Phenylhydrazone of Diethylthiocarbonic Ester and Benzoyl Chloride.—5.7 grams of the hydrazone were mixed with 3.5 grams of benzoyl chloride in the cold, when the mixture became warm and effervesced, giving off ethyl chloride. On cooling, the material was crystallized from benzene and alcohol, when small lozenge-shaped crystals were obtained melting constantly at 138°–139°. It dissolves in alkali and is precipitated unaltered by acids and a nitrogen determination gave :

	Calculated for $C_{16}H_{16}N_2O_2S$.	Found.
N	9.3	9.3

When this material is boiled with hydrochloric acid and alcohol it slowly decomposes and goes into solution. On adding sodium hydrate and crystallizing the precipitate thus produced, phenylthiolcarbazinicethyl ester melting at 112° is obtained. This same benzoyl derivative is formed when the thiolcarbazinic ester is warmed to 100° with benzoyl chloride. When it is heated with aniline, it gives carbanilide. This benzoyl derivative is in all probability *α-benzoylphenylthiolbazinicethyl ester*, $C_6H_5—N(COC_6H_5)—NHCO.SC_2H_5$.

When the above hydrazone is diluted with benzene and acetyl chloride is added, a violent effervescence takes place. The product obtained after evaporation consists of a varnish which slowly solidifies. Beyond showing that it is readily soluble in alcohol and benzene it was not further examined. The hydrazone reacts with methyl iodide in the cold and well crystallized prisms separate. These will be investigated later, it being our intention to examine other hydrazones of the carbonic esters along similar lines.

Thioncarbanilicmethyl Ester, $C_6H_5NHCS.OCH_3$.—30 grams

of phenyl mustard oil and 120 grams of methyl alcohol when boiled for 12 hours on the steam-bath, gave 29 grams of material melting at 95°–96°, after crystallizing from alcohol. This compound has recently been prepared by Orndorff and Richmond[1] and they give its melting-point at 97°. A nitrogen determination gave:

	Calculated for C_8H_9NSO.	Found.
N	8.38	8.31

This substance gives a white precipitate with thallium hydrate which becomes black on boiling. When its alcohol solution was boiled with mercuric oxide, desulphurization took place slowly and, on concentrating the solution, carbanilide was obtained.

Thiolcarbanilicmethyl Ester, $C_6H_5NHCO.SCH_3$.—2 grams of the above compound were warmed with 2 grams of methyl iodide, and the product was crystallized from alcohol, when colorless plates were obtained melting at 81°–83°. This same compound was obtained when 5 grams of phenylthionethyl carbamate was heated on the steam-bath with 10 grams of methyl iodide. A nitrogen determination gave:

	Calculated for $C_9H_{11}NSO$	Found.
N	8.38	8.44

This material gives a reddish-yellow precipitate with thallium hydrate which does not blacken on boiling (difference from the thion compound). It gives white precipitates with lead and silver nitrates, and it dissolves in concentrated sulphuric acid, and is precipitated out by water. It agrees therefore in properties with the compound obtained by Will[2] from phenylimidophenylthiocarbamicmethyl ester and sulphuric acid,

$$C_6H_5—NH—C=(NC_6H_5).SCH_3 + H_2O =$$
$$C_6H_5NHCO.SCH_3 + H_2NC_6H_5$$

Thioncarbanilicethyl Ester, $C_6H_5NHCS.OC_2H_5$, was prepared by boiling phenyl mustard oil with alcohol.[3] It was

[1] This Journal, **22**, 462.

[2] Ber. d. chem. Ges., **15**, 341.

[3] Hofmann: Ber. d. chem. Ges., **2**, 120; **3**, 773; Liebermann: Ann. Chem. (Liebig), **207**, 142, Orndorff and Richmond: This Journal, **22**, 461.

converted into *thiolcarbanilicethyl ester*, $C_6H_5NHCO.SC_2H_5$.—When 5 grams of thioncarbanilicethyl ester were heated for 12 hours with 15 grams of ethyl iodide on the steam-bath and the product crystallized from alcohol, a mass of colorless needles was obtained, melting from 71° to 73°. This compound has already been prepared by Will by a different method.[1] When boiled with a mixture of alcohol and concentrated ammonia it gave monophenylurea melting at 147°. Although this compound differs from the thion derivative by about 1° in melting-point, when portions of each are mixed, the melting-point is lowered about 35°.

Thioncarbanilicisobutyl Ester, $C_6H_5NH—CS.OC_4H_9$.—Orndorff and Richmond state that heating isobutyl alcohol and phenyl mustard oil in sealed tubes at temperatures varying from 110° to 180° gave no solid product except thiocarbanilide. They prepared this substance by heating the materials for twenty hours on the water-bath, and state that it melts at 80.5°.

We found that, when 10 grams of phenyl mustard oil and 20 grams of isobutyl alcohol were heated in a closed tube for 115° to 125° for three hours, beautiful, long, colorless prisms were obtained which, after crystallization from alcohol, melted at 77°–78°. A nitrogen determination gave:

	Calculated for $C_{11}H_{15}NSO$.	Found.
N	6.69	6.76

When 2.5 grams of the above compound were heated with 2.3 grams of isobutyl iodide in an oil-bath from 125° to 140° no action whatever was observed.

Ethyl Thioncarbamate, $H_2NCSOC_2H_5$, *and Chloracetic Acid* were mixed in molecular proportions and heated on the steam-bath until ethyl chloride ceased being evolved. The mass was then pressed on a plate, taken up in ether and filtered. The ether was then evaporated and the residue extracted with benzene. On crystallizing the material from water and ether, it melted at 135°–136° with effervescence. A nitrogen determination gave:

	Calculated for $H_2NCO.SCH_2COOH$.	Found.
N	10.37	10.20

[1] Loc. cit.

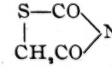
This material is therefore carbaminthioglycollic acid, $H_2NCO.SCH_2COOH$. The yield was poor, as thioglycollic acid, thiolethyl carbamate and cyanuric acid were also formed.

Isoamyl Thioncarbamate, $H_2NCSOC_5H_{11}$, *and Chloracetic Acid*, when heated on the steam-bath, deposited crystals which when crystallized from ether separated in the form of six-sided prisms melting at 123°–125° A nitrogen determination gave:

	Calculated for $C_4H_5NSO_2$	Found.
N	11.96	11.65

This material is therefore the so-called mustard oil acetic acid, or α-μ-diketotetrahydrothiazole. This compound is formed far more readily by boiling the sulphocyanacetic esters with concentrated hydrochloric acid. It can be boiled under diminished pressure without decomposition. At 19 mm. pressure it boiled from 178.5° to 179.5°.

Silver α-μ-diketotetrahydrothiazole was preparnd by precipitating the alkaline solution of the above compound with the calculated quantity of silver nitrate. It forms a light yellow powder which turns brown in the sunlight. A silver determination gave 49.8 per cent silver instead of 48.2 per cent. Hydrogen sulphide regenerates the thiazole from this salt. The same result was obtained when it was treated with benzoyl chloride.

N-Methyl-α-μ-diketotetrahydrothiazole,  .—

The above silver salt when suspended in ether and in benzene and heated for several days with methyl iodide, gave a product which boiled at 15 mm. pressure from 131° to 132°. This distillate solidified at once, on cooling, and when crystallized from benzene and ligroin, melted from 37° to 39°. A nitrogen determination gave:

	Calculated for $C_4H_5NSO_2$.	Found.
N	10.6	10.5

For purposes of comparison α-μ-diketotetrahydrothiazole was methylated according to the method employed by

Arapides[1], when a product was obtained which boiled at 14 mm. pressure from 129° to 131° and was otherwise identical with the product from the silver salt. Arapides has shown that this product has the methyl group attached to nitrogen. He states that it forms an oil which slowly solidifies over sulphuric acid and that it very readily deliquesces. This is not the case when the material is purified by distillation; it then readily solidifies and does not deliquesce on exposure.

When 1.4 gram of N-methyl-α-μ-diketotetrahydrothiazole, prepared either from the sodium or silver salt, was treated with 4.2 grams of sodium hydrate and 1.8 grams of silver nitrate added in aqueous solution, a gas was given off and a white gelatinous precipitate was obtained which turned yellow in the light. The gas was found to be carbon dioxide, and a silver determination in the precipitate gave 70.2 per cent, while the calculated percentage for silver thioglycollate $AgSCH_2COOAg$, is 70.5 per cent.

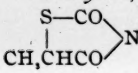
When this salt was decomposed with hydrogen sulphide, in aqueous solution, the filtrate gave with ferric chloride and ammonia the characteristic red-violet color of thioglycollic acid.

Thioncarbanilicethyl Ester, $C_6H_5NHCSOC_2H_5$, *and Chloracetic Acid* react on the steam-bath giving off ethyl chloride and water, and not hydrochloric acid and alcohol. The product when crystallized from alcohol forms long colorless needles and melts from 147° to 148°, which is the melting-point of *n-phenyl-α-μ-diketotetrahydrothiazole* (Phenylsenfölglycolid), as found by Liebermann.[2] This reaction is much smoother than in the case of ethyl thioncarbamate and chloracetic acid.

Thioncarbanilicethyl Ester and α-Brompropionicethyl Ester (by G. K. Dustin).—When 13 grams of brompropionicethyl ester were heated with one molecular proportion of thioncarbanilicethyl ester for some time on the water-bath, then for a number of hours from 120°–140°, a solid separated, on cooling. This crystallized from alcohol in groups of fine, colorless needles melting at 103° and a nitrogen determination agreed with the calculated for

[1] Ann. Chem. (Liebig), **249**, 28.
[2] Loc. cit.

n-Phenyl-α-μ-diketo-β-methyltetrahydrothiazole,



	Calculated for $C_{10}H_9NO_2S$.	Found. I.	Found. II.
N	6.7	6.7	6.6

Thioncarbanilicethyl Ester and α-Bromisobutyricethyl Ester, when heated for ten hours from 130°–155°, gave a solid, which, when crystallized from dilute alcohol, separated in the form of colorless prisms or pyramids and melted at 79°–81°. A nitrogen determination shows that this compound is *carbanil-α-thioisobutyricethyl ester*, $C_6H_5NHCO.SC(CH_3)_2CO_2C_2H_5$:

	Calculated for $C_{13}H_{17}SNO_3$.	Found.
N	5.2	4.9

This compound can be boiled with concentrated hydrochloric acid and recovered unaltered. When α-bromisobutyric acid and thioncarbanilicmethyl ester were heated as above, the only solid material isolated was aniline hydrobromide. This crystallized in plates which darkened at 245° and became black and melted with effervescence at about 280°. A bromine determination gave 46.2 per cent; calculated 45.9 per cent.

The following sulphocyan derivatives of the fatty esters $NCS—CHRCO_2R'$, are obtained in good yields by boiling the corresponding alpha-halogen esters with potassium sulphocyanide in alcoholic solution. They are oils with a penetrating, persistent, and, for the most part, disagreeable odor. They can be distilled unaltered under reduced pressure.

The boiling-points which are given in the following experiments represent the temperatures at which the greater portion of the esters were collected. For the preparation of the sulphocyanides, in some cases, the bromesters were collected under wider limits than those given in the tables, the bromesters being freshly prepared from Kahlbaum's acids by the Hell-Volhard-Zelinsky method.

Experiments by Leeds Mitchell.

Methyl Sulphocyanacetate, $NCS.CH_2CO_2CH_3$.—75 grams

of methyl chloracetate, 80 grams of absolute alcohol, and 60 grams of potassium sulphocyanide, after boiling twenty-four hours, gave 38 grams of methyl sulphocyanacetate, boiling from 120°–122° at 16 mm. pressure.

Ethyl Sulphocyanacetate boiled at 118°–122° at 15 mm. pressure. Heintz,[1] who first prepared this ester, states that it boils in a vacuum at 118°–200°, and Claesson found that it boils with partial decomposition at 225° at ordinary pressure.

Isoamyl Sulphocyanacetate boiled at 145°–147° at 17 mm. pressure, while Claesson found that it boils at 255° at ordinary pressure.

α-μ-Diketotetrahydrothiazole (*mustard-oil acetic acid*, *Senfölessigsäure*), $\begin{matrix} CH_2CO \\ | \\ S-CO \end{matrix}\!\!>\!NH$.—38 grams of methyl sulphocyanacetate and 76 grams of concentrated hydrochloric acid were boiled a few minutes until all the oil dissolved. The solution was then evaporated and the residue treated with benzene and filtered from ammonium chloride. The material dissolved by benzene was crystallized from water until it melted at 125°–126°. In this manner 2 grams of ammonium chloride and 20 grams of α-μ-diketotetrahydrothiazole were obtained. This product is identical in every respect with that obtained by heating isoamyl thioncarbamate with chloracetic acid as described above.

Experiments by Guy K. Dustin.

Methyl α-Sulphocyanpropionate, $CH_3—CH.SCN.CO_2CH_3$.—This was prepared by boiling 57 grams of methyl α-brompropionate with one molecular proportion of potassium sulphocyanide and twice its weight of alcohol until a test with ferric chloride showed no potassium sulphocyanide. This required ten hours. After filtering and evaporating the alcohol, practically the entire product boiled from 104°–106° at 15–16 mm. pressure. The yield obtained was 34 grams, while the calculated yield is 46 grams.

Nitrogen determinations gave the following results:

[1] *Loc. cit.*

	Calculated for $C_8H_7NSO_3$.	Found. I.	Found. II.
N	9.65	10.1	10.2

The material was obtained as a colorless oil with a strong, peculiar, but not unpleasant, odor.

Ethyl α-Sulphocyanpropionate.—When 30 grams of ethyl α-brompropionate were boiled with one molecular proportion of potassium sulphocyanide, it required two days before the action was complete. On distilling the reaction-product at 16 mm. pressure it all boiled at 104°–110°, mostly at 107°–108°. The yield was 22 grams and an analysis of the colorless oil thus obtained gave :

	Calculated for $C_6H_9NSO_3$.	Found.
N	8.8	8.9

Isobutyl α-Sulphocyanpropionate was obtained when 71 grams of isobutyl α-brompropionate was boiled in alcoholic solution with 33 grams of potassium sulphocyanide. On distilling at 15 mm. pressure, 38 grams of clear, colorless oil, boiling at 130°–131° were collected, the odor of which was not unpleasant. A nitrogen determination gave :

	Calculated for $C_8H_{13}NSO_3$.	Found.
N	7.48	7.48

Isoamyl α-Sulphocyanpropionate was prepared by boiling 87 grams of the brom ester with potassium sulphocyanide and alcohol for seven hours. It boiled at 141°.5 at 15 mm. pressure, and the yield was 67 grams. It was thus obtained as a colorless oil, the odor of which was not unpleasant. A nitrogen determination gave :

	Calculated for $C_9H_{15}NSO_3$.	Found.
N	6.9	7.0

When this oil is distilled at ordinary pressure it boils with decomposition at 265°–267°.

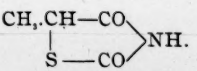
The boiling-points of the α-brompropionic esters used in making the above sulphocyan derivatives were as follows :

The *methyl ester* boiled at 51°.5 at 19 mm. pressure.

The *ethyl ester* boiled at 56°–58° at 14 mm. pressure.

The *isobutyl ester* boiled at 79°–80° at 14 mm. pressure.

The *isoamyl ester* boiled at 99°–100° at 16 mm. pressure.

β-Methyl α-μ-Diketotetrahydrothiazole, 

—The best yield of this substance was obtained from the methyl ester. 11 grams of methyl α-sulphocyanpropionate and 15 grams of concentrated hydrochloric acid were mixed and evaporated to dryness on the steam-bath. Benzene then removed 0.6 gram of ammonium chloride, and 7.8 grams of crude thiazole were obtained. This, when crystallized from a mixture of benzene and ligroin, separated in the form of colorless leaves and melted from 46°–47°, and nitrogen determinations gave the following:

	Calculated for $C_4H_5NSO_2$.	Found. I.	II.
N	10.6	10.5	10.5

On distilling it at 20 mm. pressure it boiled, for the most part, from 165°–168°. Silver nitrate added to the alkaline solution of this substance produces a bulky, white, but not gelatinous ,precipitate of the silver salt. It is decomposed by warm water.

Experiments by Harry LeB. Gray.

Methyl α-Sulphocyanisobutyrate, $(CH_3)_2C.SCN.CO_2.CH_3$, was obtained in a similar manner to the preceding sulphocyanides as a heavy, colorless oil having a disagreeable, penetrating odor. It boiled for the most part from 101°–102° at 17 mm. pressure. This fraction was analyzed with the following result:

	Calculated for $C_6H_9NSO_2$.	Found.
N	8.8	8.9

Ethyl α-Sulphocyanisobutyrate resembles the methyl ester in properties. The greater portion boiled at 111°–115° at 22 mm. pressure. A nitrogen determination gave:

	Calculated for $C_7H_{11}NSO_2$.	Found.
N	8.09	8.68

Isobutyl α-Sulphocyanisobutyrate.—The product in this case, after several distillations, boiled at 132°–133° at 21 mm. pressure. This fraction gave the following result on analysis:

	Calculated for $C_9H_{15}NSO_3$.	Found.
N	6.96	6.90

Isoamyl α-Sulphocyanisobutyrate, on fractioning, boiled at 135°.5–136°.5 at 16 mm. pressure. A nitrogen determination gave:

	Calculated for $C_{10}H_{17}NSO_3$.	Found.
N	6.5	7.1

This material, like the preceding, is a colorless oil with a penetrating, disagreeable odor.

The boiling-points of the α-bromisobutyric esters used in making the above sulphocyan derivatives were as follows:

The *methyl ester* boiled at 51°–52° at 19 mm. pressure.

The *ethyl ester* boiled at 70°–71° at 20 mm. pressure.

The *isobutyl ester* boiled at 83°–85° at 16 mm. pressure.

The *isoamyl ester* boiled at 107°–108° at 25 mm. pressure.

β-Dimethyl α-μ-Diketotetrahydrothiazole, $(CH_3)_2C(CO)(S-CO)NH$.—The best yield of this substance was obtained from the methyl ester; the amyl ester failed to give the compound. Fourteen grams of methyl α-sulphocyanisobutyrate were mixed with 20 cc. concentrated hydrochloric acid and heated on the steam-bath for about one hour. The reaction is complete when no more oil remains on the surface of the liquid. The solution, when evaporated, gave 1 gram of ammonium chloride, the remaining material being the thiazole derivative. This crystallizes from water in enormously lengthened, colored prisms, one crystal being obtained that measured 31 mm. long and 1.5 mm. in diameter. It melts at 79°–80°, and a nitrogen determination gave:

	Calculated for $C_4H_7NSO_2$.	Found.
N	9.65	9.87

Experiments by Henry A. North.

Methyl α-Sulphocyanbutyrate, $C_2H_4CH.SCN.CO_2CH_3$.—This was obtained as a colorless oil boiling at 125° at 23 mm. pressure, and a nitrogen determination gave the following result:

	Calculated for $C_8H_9NSO_2$.	Found.
N	8.8	8.6

Ethyl α-Sulphocyanbutyrate.—On mixing 100 grams of the bromester, 49.6 grams of potassium sulphocyanide, and 200 cc. of alcohol, and boiling for twelve hours, somewhat more than 65 grams of a clear, colorless oil was obtained. This boiled from 134°–136° at 28 mm. pressure. Like the other members of this series, it has a strong, unpleasant, extremely persistent odor. A nitrogen determination gave the following result:

	Calculated for $C_6H_{11}NSO_2$.	Found.
N	8.09	8.35

Isoamyl α-Sulphocyanbutyrate was obtained as a colorless oil which, after fractionation boiled from 158° to 160° at 23 mm. pressure. A nitrogen determination gave:

	Calculated for $C_{10}H_{17}NSO_2$.	Found.
N	6.51	6.37

The boiling-points of the α-brom normal butyric esters used in making the above sulphocyan derivatives were as follows:

The *methyl ester* boiled at 67°–72° at 25 mm. pressure.

The *ethyl ester* boiled at 68°–69° at 19 mm. pressure.

The *isoamyl ester* boiled at 110.5°–113.5° at 19 mm. pressure.

β-Ethyl α-μ-Diketotetrahydrothiazole, $C_2H_5CH\begin{<}\begin{matrix}CO\\ |\\ S-CO\end{matrix}\end{>}NH.$—

This is best obtained from the methyl or ethyl esters. On warming these with concentrated hydrochloric acid, until solution took place and then evaporating, a colorless oil was obtained which solidified on cooling. When crystallized from a mixture of benzene and ligroin, six-sided prisms separated which finally melted from 63° to 65°, and a nitrogen determination gave the following result:

	Calculated for $C_5H_7NSO_2$.	Found.
N	9.65	9.68

Experiments by W. H. Buell.

Methyl α-Sulphocyanisovalerianate, $(CH_3)_2CH—CH.SCN.CO_2CH_3$.—39 grams of the brom ester, 78 grams of alcohol and 19.4 grams of potassium sulphocyanide, warmed on the water-bath for two days, gave 14 grams of colorless oil boiling from 119° to 121.5° at 23 mm. pressure. It has a peculiar penetrating unpleasant odor. A nitrogen determination gave:

	Calculated for $C_7H_{11}NSO_2$.	Found.
N	8.09	8.35

Ethyl α-Sulphocyanisovalerianate.—88 grams of the brom ester, 40.8 grams of potassium sulphocyanide and 176 grams of alcohol were boiled for three days. On fractioning, 34 grams of ester were obtained, boiling from 126° to 128° at 19 mm. pressure. This was analyzed with the following result:

	Calculated for $C_8H_{13}NSO_2$.	Found.
N	7.48	7.85

Isobutyl α-Sulphocyanisovalerianate.—55 grams of the brom ester, 22.5 grams of potassium sulphocyanide and 110 grams of alcohol gave 19 grams of oil, boiling, for the most part, from 145° to 147° at 19 mm. pressure. This gave the following result on analysis:

	Calculated for $C_{10}H_{17}NSO_2$.	Found.
N	6.5	5.8

This ester, like the above, had a strong, peculiar odor which, perhaps, was not unpleasant.

Isoamyl α-Sulphocyanisovalerianate.—105 grams of the brom ester, 210 grams of alcohol and 40.6 grams of potassium sulphocyanide gave a colorless oil with a disagreeable odor after boiling for two days. The greater portion of this boiled from 151° to 152° at 14 mm. pressure and a nitrogen determination gave the following result:

	Calculated for $C_{11}H_{19}NSO_2$.	Found.
N	6.11	6.32

The boiling-points of the α-bromisovalerianic esters used in making the above sulphocyan derivatives were as follows:

The *methyl ester* boiled from 174°–182° at 760 mm. pressure.

The *ethyl ester* boiled from 186°–187° at 764 mm. pressure.

The *isobutyl ester* boiled from 105°–108° at 17 mm. pressure.

The *isoamyl ester* boiled from 113°–114° at 16 mm. pressure.

When the above sulphocyanic esters were boiled with hydrochloric acid the products were oils in each case. The ethyl ester gave a product which solidified in a freezing-mixture, but, on attempting to crystallize it, or on removing it from the freezing-mixture, it became liquid, and, on attempting to distil it under diminished pressure, it decomposed.

For convenience of reference, the boiling-points of the sulphocyanic esters, described by us, are collected in the following table:

	Pressure in mm.	Boiling-point.
Methyl α-Sulphocyanacetate	16	120°–122°
Ethyl "	15	118°–122°
Isoamyl "	17	145°–147°
Methyl α-Sulphocyanpropionate	15–16	104°–106°
Ethyl "	16	107°–108°
Isobutyl "	15	130°–131°
Isoamyl "	15	141.5°
Methyl α-Sulphocyanisobutyrate	17	101°–102°
Ethyl "	22	111°–115°
Isobutyl "	21	132°–133°
Isoamyl "	16	135.5°–136.5°
Methyl α-Sulphocyanbutyrate	23	125°
Ethyl "	28	134°–136°
Isoamyl "	23	158°–160°
Methyl α-Sulphocyanisovalerianate	23	119°–121.5°
Ethyl "	19	126°–128°
Isobutyl "	19	145°–147°
Isoamyl "	14	151°–152°

NEW HAVEN, CONN., April 3, 1900.

THE CONDUCTIVITY TEMPERATURE COEFFICIENT OF SOME LIQUID AMMONIA SOLUTIONS.

By Edward C. Franklin and Charles A. Kraus.

It was first established by Kohlrausch[1] that the electrical conductivity of aqueous solutions of electrolytes increases with the temperature, and that for ordinary temperatures this relation may be represented by the linear function,

$$\lambda_t = \lambda_o (1 + bt).$$

Arrhenius,[2] however, from theoretical considerations, has shown that the relation between temperature and conductivity is not a linear one, but that the conductivity at first increases with the temperature, reaches a maximum value, and then decreases. He deduced an exponential equation to represent the relation between temperature and conductivity and found by experiment that in the case of hypophosphorous acid and phosphoric acid his calculated maximum temperatures agree with his observations. He calculated the maxima for a number of salts, acids, and bases, but the temperatures of maximum molecular conductivity generally lie too high for experimental verification.

Further investigations upon the effect of changes of temperature on the conductivity of aqueous solutions have been made by Trötsch,[3] Krannhals,[4] Sack,[5] Schroeder,[6] Rudolphi,[7] Euler,[8] Bauer,[9] and Schaller.[10]

Since the measurements of Arrhenius on phosphoric acid and hypophosphorous acid, maxima of conductivity have been established for solutions of copper sulphate and of a number of organic acids, while according to the investigations of Cattaneo[11] all ethereal solutions of electrolytes and alcoholic

1 Pogg. Ann., **154**, 228 (1875).
2 Ztschr. phys. Chem., **4**, 96 (1889).
3 Wied. Ann., **41**, 256 (1890).
4 Ztschr. phys. Chem., **5**, 250 (1890).
5 Wied. Ann., **43**, 212 (1891).
6 Ztschr. phys. Chem., **16**, 72 (1895).
7 *Ibid.*, **17**, 377 (1895).
8 *Ibid.*, **21**, 257 (1896).
9 *Ibid.*, **23**, 409 (1897).
10 *Ibid.*, **25**, 497 (1898).
11 Beibl. Wied. Ann., **18**, 219, 365 and 1085 (1894).

solutions of the bromides and iodides exhibit negative temperature coefficients.

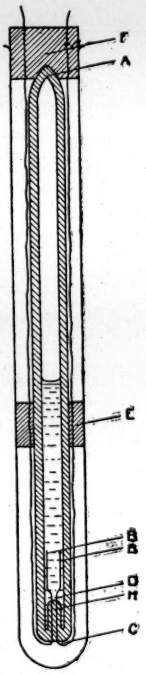
Most of the measurements made by the investigators mentioned above are confined to temperatures below 52°, some of them reach 100°, while only those of Sack on copper sulphate exceed this temperature. Sack followed the conductivity of copper sulphate solution to 124° when his conductivity cell exploded. A very serious obstacle to carrying such measurements to higher temperatures is the solvent action of the water on the glass resistance vessel, which even at 100° becomes so great as seriously to interfere with the accuracy of the measurements. Certainly at temperatures from 100° to 200° or more above the boiling-point of water, temperatures which must be reached if the maxima predicted by Arrhenius are to be realized, the action of the solvent on the resistance cell would be so great as to prohibit even approximate measurements of conductivity. Furthermore, the very high tension of aqueous vapor at elevated temperatures, and especially at temperatures approaching the critical point, must render difficult the adaption of conductivity vessels for the purpose.

In ammonia, however, we have found an electrolytic solvent which lends itself much better to measurements of the conductivity of its solutions at temperatures far above its boiling-point at atmospheric pressure. The fact that it does not dissolve the materials of the glass vessels used eliminates at once a very serious obstacle in the way of such measurement, when water is used as the solvent. The temperatures of maximum conductivity lie below the ordinary temperature, which has enabled us to follow easily the negative branch of the curve for a considerable distance beyond the maximum, and even beyond the critical temperature of the solvent; conditions which would probably be difficult to control in the case of water.

The Conductivity Vessel.

Conductivity cells of the form indicated in the adjoining figure were devised and used in making the measurements recorded in this paper. The cell *A* is made of heavy-walled

glass tubing. *BB* are the electrodes, each of about 1 sq. cm. area. The leading-in wires, *C*, are of very fine platinum wire for the reason that tubes with larger wire invariably burst at high temperatures, especially as the pressure approached the critical pressure of the ammonia. At *D* sufficiently heavy wire was used to retain the electrodes in position. *E* and *F* are corks for holding the tube *A* in position within the outer thin-walled tube, which latter served the purpose of protecting the leading-in wires from injury. The conductivity tube thus protected was suspended in the temperature bath by means of the heavier copper connecting wires.



After platinizing the electrodes the resistance capacity of the cell was measured by means of a fiftieth-normal solution of potassium chloride. The tube was then cleaned, dried, and weighed. A weighed quantity of the solute was then placed in the tube and the air displaced by a slow current of ammonia gas from the stock cylinder. While maintaining the current of gas the tube was placed in a bath of liquid ammonia contained in a vacuum-jacketed test-tube, and liquid ammonia was drawn from the stock cylinder in the manner described in a previous paper,[1] until the liquid occupied from about one-third to one-half of the volume of the conductivity tube. The tube was then sealed off before the blow-pipe. The portion of the tube drawn off in sealing was preserved and weighed together with the sealed tube and its contents. The weight of ammonia contained in the tube was found by subtracting from the weight thus obtained, the weight of the empty tube plus the weight of the solute. It was not attempted in these preliminary experiments to determine the volume of the solution at the different temperatures. The

[1] This JOURNAL, **20**, 839 (1898).

volume used in calculating the results given below was obtained by dividing the weight of ammonia contained in the tube by its specific gravity at its boiling-point ; *viz.*, 0.68.[1]

Method of Making the Determinations.

The bridge and telephone method of Kohlrausch was used for measuring the resistances. For measurements at low temperatures the conductivity tube was immersed in a bath of carbon dioxide and ether contained in a vacuum-jacketed tube. The bath was allowed to warm up slowly and the temperatures were read at intervals of from 2°–10° by means of an air thermometer. For the higher temperatures a paraffin bath and a mercury thermometer were used.

The following results have been obtained :

Ammonium Iodide.

Weight of solute, 0.00830 gram.
" " solvent, 1.967 grams.
Cell constant, 0.1514.
Dilution, *v*, 50.76.

T.	μ_t	T.	μ_t
235	162.9	302	223.1
242	170.8	305	225.9
248	177.7	308	227.3
253	186.8	312	224.9
261	194.5	318	224.2
268	204.2	326	215.2
275	211.5	335	207.7
281	216.1	344	197.1
285	219.6	353	181.4
291	221.5	364	158.9
299	223.1		

Ammonium Bromide.

Weight of solute, 0.01365 gram.
" " solvent, 1.4965 grams.
Cell constant, 0.1571.
Dilution, *v*, 15.79.

[1] Lange : Ztschr. gesamt. Kält-Indust., **5**, 1 (1898).

T.	μ_t.	T.	μ_t.
241	103.8	364	60.8
250	106.5	373	55.1
261	110.2	383	44.9
274	112.9	390	38.2
283	113.7	395	26.5
294	110.6	367	47.6
298	109.0	373	41.9
308	106.0	383	30.4
318	101.8	390	22.7
327	95.8	395	17.7
336	86.1	401	7.96
344	83.0	405	4.97
354	72.3	406	2.93

Ammonium Chloride.

Weight of solute, 0.01157 gram.
" " solvent, 2.122 grams.
Cell constant, 0.1548.
Dilution, v, 14.43.

T.	μ_t.	T.	μ_t.
235	70.9	277	77.5
245	73.0	279	76.9
248	73.9	285	76.0
253	74.5	290	75.3
257	75.1	292	73.9
262	76.0	295	72.1
267	76.6	298	68.8
273	76.6		

Potassium Iodide.

Weight of solute, 0.00121 gram.
Volume of solvent, 2.5 cc., approximate.
Cell constant, 0.1533.
Dilution, v, 34.30.

T.	μ_t.	T.	μ_t.
205	104.9	298	196.8
210	119.0	303	194.3
220	128.0	307	192.8
230	143.7	314	187.5
240	159.1	324	174.0
251	175.4	335	160.6
261	185.6	347	156.3

T.	μ_t.	T.	μ_t.
271	193.2	355	128.9
281	196.7	360	120.4
283	199.1	364	112.1
288	199.8	370	101.0
294	198.4	373	82.6

Paranitrophenol.

Weight of solute, 0.00571 gram.
" " solvent, 1.868 grams.
Cell constant, 0.1956.
Dilution, v, 67.07.

T.	μ_t.	T.	μ_t.
252	160.2	312	194.7
259	166.1	316	189.0
267	174.2	323	184.6
276	182.8	333	174.4
290	192.2	343	154.1
298	192.6	354	134.0
303	194.4	363	109.7

Copper Nitrate.

Weight of solute, 0.01068 gram.
" " solvent, 1.108 grams.
Cell constant, 0.2343.
Dilution, v, 28.51.

T.	μ_t.	T.	μ_t.
211	72.2	284	106.3
214	73.9	287	105.5
216	75.2	292	104.6
221	79.7	298	103.2
229	85.2	306	103.4
237	91.9	315	98.2
246	96.6	323	91.4
255	102.7	332	88.0
261	105.5	343	81.9
271	106.3	352	74.0
277	106.8	359	70.0

As this solution was heated up to higher temperatures there was deposited on the walls of the tube a slightly colored solid, which, as the critical temperature was approached, melted and flowed to the bottom of the tube as a blue liquid, leaving

the solution colorless. On cooling, the liquid diffuses through the solution, the latter thus regaining its original blue color. The conductivity of the solution after cooling was found to have increased considerably, due probably to chemical action between the solvent and solute. At 140°, 7° above the temperature at which the meniscus had disappeared, the solution remained distinctly a conductor.

Sulphur.

Sulphur dissolves in ammonia to form a colored solution which is a fair conductor of electricity. What the substance is which is formed and acts as an electrolyte has not yet been investigated. As the solution was heated the conductivity increased until the temperature of 60° was reached. On repeating the experiment with the same tube later the conductivity of the solution was found to be much higher and the maximum was this time located at 17° instead of at 60°, as in the first experiment. This change of conductivity probably indicates chemical action between the solute and solvent. At temperatures above the maximum the conductivity decreased with increasing temperature reaching a value of 1.04 at 139°, 6° above the critical temperature of ammonia.

Weight of solute, 0.00280 gram.

" " ammonia, 1.987 grams.

Cell constant, 0.1296.

Dilution, v, 53.5.

T.	μ_t	T.	μ_t
238	74.6	348	61.3
248	80.9	359	51.3
255	83.5	373	36.8
264	86.0	381	31.5
273	87.7	389	21.7
283	88.8	393	17.0
292	88.8	400	9.14
298	88.2	404	4.44
301	86.5	407	1.79
312	83.6	411	1.11
324	78.2	412	1.04
334	72.0		

In order to determine definitely whether or not the solution retains its power as a conductor above its critical temperature

and after the complete disappearance of the meniscus, the conductivity tube was slowly warmed up from 121° to 139°.5. The temperature rose very gradually during seven hours, which was the time used in making the series of measurements. At 139°.5, 6°.5 above the critical temperature, the solution still showed a distinct conductivity; *viz.*, 0.65 Kohlrausch unit.

	T.	μ_t.	
1 P.M.	394	13.6	
	400	7.71	
	403.7	3.79	
	406	1.58	(1)
	409.1	0.95	(2)
	410	0.82	(3)
8 P.M.	412.5	0.65	

(1) The meniscus gradually faded until it was impossible to detect the slightest optical difference between liquid and vapor excepting color, the latter appearing to fill the tube up to the point at which the meniscus disappeared. The color line was not sharply defined. No perceptible amount of solute had precipitated out. The conductivity fell to 1.58 and then, as the temperature fell through about 0°.1, again increased slightly.

(2) The color had diffused until it filled the tube to within a short distance of the top. No solute had separated from the solution.

(3) The color had diffused through the whole tube, the color at the top, however, being weaker than lower down the tube.

Temperature Coefficient of Solution of Potassium Iodide in Methylamine.

Preliminary experiments upon the properties of methylamine showed it to be a good solvent for a number of metallic iodides and bromides. It also dissolved sugar abundantly. The limited quantity of the solvent at our disposal prevented an extension of these tests. The solution of potassium iodide in methylamine was found to be a fair conductor of electricity as is shown by the results given in the following table:

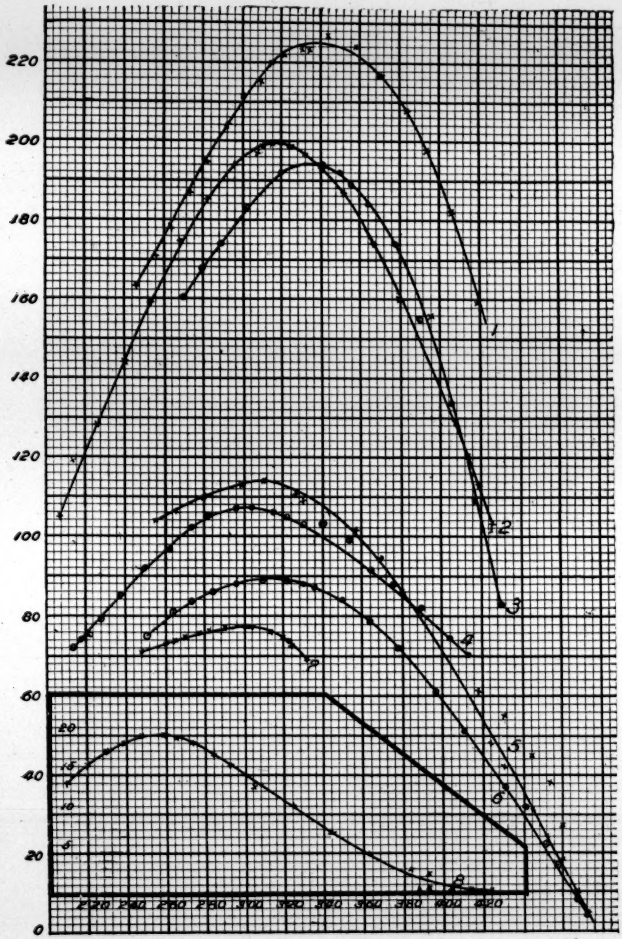
Weight of solute, 0.0306 gram.
Volume of solvent, 1.9 cc. approximate.
Cell constant, 0.0969.
Dilution, v, 10.31.

T.	μ_t.	T.	μ_t.
210	14.10	303	13.38
221	15.99	323	11.59
230	17.75	343	7.33
239	19.39	363	4.71
249	20.14	383	3.02
258	20.22	393	2.66
266	19.74	393	0.81
276	18.57	404	0.33
283	17.42	413	0.17
293	15.99	423	0.12

Temperature Coefficient of Solutions of the Alkali Metals.

Liquid ammonia acts slowly on metallic sodium in solution with evolution of hydrogen and the formation of sodamide even at 80° below zero. This action between solvent and solute has so far prevented accurate measurements of the temperature coefficient of the solution. In order to obtain an approximate value of the temperature coefficient a solution of sodium was sealed up in a conductivity tube, and placed in a bath of carbon dioxide and ether. After the resistance had become approximately constant the bath was allowed to warm up gradually. This was accompanied by an increase in the conductivity of the solution of about 0.6 per cent per degree. On cooling the tube again the conductivity does not return to its original value. With rising temperature the conductivity continues to increase until the effect of rising temperature is overcome by the removal of metal from solution. The conductivity then falls away until the metal has completely disappeared and the solution takes on the conductivity of the sodamide solution.

For example, one experiment on a solution of sodium gave the following results: At a temperature of 191° absolute, the resistance of the solution in a sealed tube was 8.05 ohms. On slowly warming the tube the resistance fell until a minimum value of 5.92 ohms was reached at 232°. Then as the temperature continued to rise the resistance also increased. On



Graphical Representation of Results.

rapidly cooling to 220° the resistance increased to 7.63 ohms. As the bath again warmed up, the resistance fell, passed a minimum, and then increased. After a time the reaction between the metal and the solvent was complete, as was indicated by the entire disappearance of the blue color of the metal solution. The solution then showed the much higher resistance of the solution of sodamide.

Solutions of metallic lithium and potassium also show positive temperature coefficients. These metals also react with the solvent, lithium more slowly and potassium much more rapidly than sodium.

The results of the measurements given in this paper are plotted in the accompanying plate, the temperatures being plotted as abscissae and conductivity as ordinates. It is apparent from the curves that the maxima of all the solutions studied lie above the boiling-point of the solvent and not very far apart. The curves are similar in shape on both sides of the maxima. In the case of those solutes which evidently do not enter into reactions with the solvent, the curves approximate very closely to the parabola. The curves tend toward zero in the neighborhood of 133°, the critical temperature of ammonia.

Summary.

I. Liquid ammonia is a solvent which lends itself to measurements of temperature coefficients of its solutions.

II. Measurements on the solutions of eight electrolytes at increasing temperatures show them all to pass through maxima of conductivity.

III. Solutions in liquid ammonia retain the power of carrying the electric current up to and beyond the critical temperature of the solution.

IV. Solutions of potassium, sodium, and lithium in ammonia exhibit positive temperature coefficients.

V. Methylamine is an electrolytic solvent.

The results so far obtained are but preliminary and are published at this time for the reason that it is not possible for the authors to continue the work together. The investigations will be continued by one of us.

THE UNIVERSITY OF KANSAS,
LAWRENCE, Summer of 1899.

OBITUARY.

EDOUARD GRIMAUX.

Edouard Grimaux, whose death occurred May 31, 1900, was born in 1835 at Rochefort-sur-Mer. He was originally connected with the marine sanitary corps, but gave up this profession and went to Paris, to study under Wurtz, about the time when the modern theories of chemistry were furnishing a battlefield for the supporters of the new and the old theories. He took his medical degree in 1865, and became assistant in 1872 and adjunct professor in 1874 in the École polytechnique. He succeeded Cahours as Professor, and in 1894 succeeded Fremy in the Académie des Sciences. He was especially interested in the synthetical side of chemistry and was the author of a number of works on chemistry among which were "Equivalents, Atoms, and Molecules"; "Organic Chemistry"; "Inorganic Elementary Chemistry"; "Theoretical Chemistry"; and "Letters, Manuscripts, Private and Collected Papers of Lavoisier." He was removed in 1898, by the Minister of War, from his position as Professor in the École polytechnique, on account of his participation in the Zola affair.

J. E. G.

ADOLF CLAUS.

Any discussion of the interesting, but as yet unsettled, question of the structure of benzene, will necessarily introduce the name of Adolf Claus, whose death occurred May 4th. He suggested and always strongly supported the diagonal formula of benzene and was one of the first to recognize the importance of an understanding of the structural relationship of chemical compounds. He was born in Cassel, June 6, 1838, and, after studying under Kolbe in Marburg and Wöhler in Göttingen, went to Freiburg as assistant to von Babo. His life as a teacher and investigator was spent at this University, where he became Privatdocent in 1863, Associate Professor in 1867, and Professor in 1875. Among the several hundred papers he has published, in conjunction with his students, are those on the relation between oximes and ketones and the isomerism of related compounds, on alkaloids, on the constitution of benzene and naphthalene, on questions of stereoisomerism in a number of cases, on tautomerism, and on many other questions concerning, especially, the aromatic compounds.

J. E. G.

NOTES.

On Krypton.

In a paper recently communicated to the Berlin Academy of Sciences, Ladenburg and Kruegel give an account of some work done by them on krypton (Chem. News, **81**, 205, 1900). About 3 liters of the residue obtained by evaporating 850 liters of liquid air were used. It was allowed to evaporate slowly, the gas being collected in large gasometers. This large volume of gas (2300 liters) was then freed from oxygen by being passed over heated copper. "From the remaining 120 liters the nitrogen was separated by essentially the methods mentioned by Lord Rayleigh and Ramsay for the isolation of argon." The last traces of nitrogen were removed by sparking over caustic soda with an excess of oxygen. The latter was absorbed by pyrogallol and soda. The gas (3.5 liters) was then dried by means of phosphorus pentoxide and collected in exhausted Ramsay gasometers (Ztschr. physikal. Chem., **28**, 247). By means of liquid air it was condensed to a colorless liquid in which floated small numbers of colorless crystals. The liquid was allowed to boil, the gas being collected in five receivers. The larger part (2.5 liters) boiled at about —181.2°. At —153° the last portions of liquid evaporated, leaving behind the crystals which melted at —149°, and then quickly evaporated. The gas obtained from the boiling liquid was found to be a mixture of krypton and argon, in which the latter predominated. The gas obtained from the crystals gave a strong krypton spectrum, together with some doubtful lines that may have belonged to argon, although the characteristic line of that substance (603.3 mm.) was absent. In comparing the spectra it was found that ten lines of their krypton spectrum were identical with those of the argon spectrum, but several of the fainter argon lines, together with the whole violet end of the argon spectrum do not occur in the krypton spectrum. "One must conclude therefrom that either very little argon or only a constituent part of argon is contained in our krypton."

The density of the gas was found to be 58.81 (O = 32) with a probable error of 1 per cent. To control this determination the gas was again sparked with oxygen, the latter was removed by pyrogallol, and the gas was collected over mercury and allowed to stand nearly two days over yellow phosphorus and fused caustic soda. Its density was then found to be 58.67. "Therefrom it follows with certainty that the krypton contained no more oxygen, and since very little argon was

mixed with it, as already inferred from the spectrum examination, one may well consider it as nearly pure. This conclusion is essentially supported by the fact that the gas originated from a crystalline body which doubtless speaks for its not being a mixture." They suggest placing the new gases of the air in the first group in Mendeléef's table, thus: He = 4 before lithium; Ne = 20 before sodium; A = 39 before potassium; and Kr = 59 before copper. "Still this is only a hypothesis which requires further testing." C. E. W.

Metallic Calcium and Some of Its Compounds.

In a recent number[1] of the "Annales de Chimie et de Physique," Moissan describes several methods for the preparation of pure metallic calcium in quantity. As a result of a thorough study of all the methods which had been previously used, and of his experiences with the electric furnace, the author recommends two methods for the preparation of this metal. The first method consists in heating a mixture of anhydrous crystallized calcium iodide and metallic sodium in an iron crucible with a screw top. This was heated for an hour at a low red heat. The condensation of the sodium vapors in the threads of the screw soon made the vessel air-tight and the calcium dissolved in the molten sodium and crystallized when the mass cooled. In order to separate the calcium, the mass was broken up and treated, *in small portions*, with absolute alcohol, which had been freed from air and saturated with pure dry hydrogen, until a portion of the alcohol, when evaporated, left no deposit. It was then washed with anhydrous ether and dried in a current of dry carbon dioxide and hydrogen. In the second method advantage was taken of the fact that calcium oxide, when heated with carbon, is decomposed with the formation of metallic calcium and oxides of carbon. Under ordinary conditions the metallic calcium decomposes the oxides of carbon to form the oxide and carbide; but if an iron tube, of which the part beyond the furnace is surrounded by a lead condenser through which cold water passes, is introduced into one side of the furnace and another tube on the opposite side, for introducing hydrogen, the gases formed can be swept out into the condenser and cooled before they have an opportunity to react upon one another. By this method a mixture of metallic calcium and the hydride is obtained and the pure calcium extracted from this mixture.

The pure calcium is soft and can be cut with a knife like sodium. If entirely free from contact with nitrogen its surface is bright and of the color of silver. It is one of the most ac-

[1] Ann. chim. phys. (7), **18**, 289.

tive elements known and combines with all the others except argon. It combines with fluorine at ordinary temperature, and burns in oxygen at 300° with the formation of heat sufficient to volatilize the calcium oxide, a phenomenon only observed in the electric furnace. It combines with hydrogen to form the hydride CaH_2, and burns brilliantly in the air, forming compounds with both the oxygen and nitrogen. It decomposes water easily and even with incandescence, if it is in the form of powder. It reduces the oxides of boron and silicon, and displaces sodium and potassium from their hydroxides, at red heat. The compound formed by passing pure dry hydrogen over the metallic calcium, which is heated in a glass tube, is especially interesting on account of its great stability. It is not decomposed when heated in a vacuum at 600°, in hydrogen to the temperature at which Bohemian glass fuses, nor when heated in air on platinum foil. It, however, burns in pure oxygen at a red heat. No solvent has been found for it. In preparing this substance only small quantities of the calcium can be used at one time, as the heat generated in the action is sufficient to reduce the silicon compounds of the glass, forming a dark layer on the inside of the tube. It decomposes the chlorides of the alkalies, setting the latter free at a red heat, and decomposes oxidizing agents, sometimes accompanied by a violent reaction. It acts on water, liberating hydrogen, of which one-half comes from the water and one-half from the hydride. The compound of the composition Ca_3N_2, which is formed when the calcium is heated in nitrogen, resembles bronze in color. It burns in air with incandescence, and forms the hydride and ammonia when heated in hydrogen. The decomposition with water, to form the hydroxide and ammonia, suggested the possibility of using this method for the preparation of ammonia from the nitrogen of the atmosphere; but under present conditions this method is not practical, although a great step in this direction has been made in this investigation.

A new phosphide, Ca_3P_2, has been obtained by heating calcium phosphate, in the electric furnace under carefully regulated conditions. If the heating is continued too long the phosphide is decomposed with loss of phosphorus. The phosphide melts only in the electric furnace; but dissociates slowly in a vacuum at the temperature at which Bohemian glass melts. If the heating, when the phosphide was formed, was carried far enough, the product of the decomposition with water was pure phosphine, whereas the product formed by insufficient heating generates some liquid phosphine with water.

An interesting fact, which was discovered in the course of

this work, is that pure calcium carbide, made from the pure metal, is perfectly transparent and white, the ordinary appearance being due, as was shown by experiment, to small traces of iron. A determination of the heat of formation of calcium oxide, made with the pure metal, gave the value 145 cal., a figure more in agreement with the facts observed, than the value 131.5 cal., obtained by Thomsen. The value obtained in this case, when compared with those of $K_2O = +98.2$ cal. and $Na_2O = +100.9$ cal. furnishes an explanation of the replacement of the alkalies by calcium and suggests the possibility of replacing the lithium in Li_2O, whose heat of formation is $+141.2$ cal., a figure also below that of calcium. Experiment showed that lithium could easily be replaced by calcium, thus supporting the theoretical deduction. J. E. G.

On Radioactive Barium.

Béla v. Lengyel[1] has just published a preliminary notice on the preparation of radioactive barium. Five radioactive elements are now known, uranium, thorium, polonium, radium, and Debierne's element resembling titanium in its chemical properties. Of these, with the exception of uranium and thorium, radium has been most studied. Evidence from its atomic weight and from its spectrum point to its being an element, but the author thinks that such evidence is insufficient. Further, he calls attention to the fact that three new so-called elements, differing only in their radioactivity from well-known elements, have been obtained from one substance, pitchblende.

Such considerations led the author to investigate the question whether radioactive substances contain new elements. In order to answer this question he decided to prepare radium synthetically, if possible. It is evident that if ordinary inactive barium chloride could be transformed into radioactive barium chloride, the problem would be solved. His investigations have led to positive results. He has succeeded in preparing a radioactive barium chloride which possesses all the properties of radium as observed by different investigators.

His method of procedure was as follows: Uranyl nitrate is melted with 2–3 per cent of barium nitrate, the nitric acid driven off as much as possible by heat, and the remaining oxides melted in the electric arc. The melt is dissolved in nitric acid, and the solution concentrated by evaporation, whereupon a large part of the barium separates out as the nitrate. The hot solution is then decanted from the crystals and to it is added three or four times its mass of water. Now

[1] Ber. d. chem. Ges., 33, 1237.

the radioactive barium sulphate is precipitated with sulphuric acid. In this way only a small amount of sulphate is obtained in comparison with the amount of barium nitrate used. Twenty grams of barium nitrate yielded 3–5 grams of the radioactive sulphate contaminated with a large amount of ordinary barium sulphate. From the sulphate the radioactive chloride and carbonate were prepared. The author says that the sulphate is nearly white with a slight yellowish tinge, due probably to a trace of uranium.

The radioactive sulphate, chloride, and carbonate thus prepared produced impressions on photographic plates and rendered gases conductors of electricity.

These experiments are not sufficient to decide the question whether or not radium is an element, but they render its existence doubtful.

The author expects to continue his investigations on this subject. C. E. C.

On Sulphur Perfluoride, SF_6.

Moissan and Lebeau[1] have shown that, when sulphur is introduced into an excess of fluorin in a glass tube over mercury, the sulphur burns with a brilliant flame. After the reaction is over, two gases are found to be present; one of these is insoluble in water, but is absorbed by a solution of potassium hydroxide, while the other is not absorbed either by water or potassium hydroxide, and is decomposed by the vapor of sodium only at the temperature of the boiling-point of the latter.

By repeating the experiment with varying proportions of sulphur and fluorine, it was found that the two fluorides are always formed, but that, when there is an excess of fluorine present, the insoluble gas is formed in larger proportion, sometimes amounting to 90 per cent. The insoluble gas is easily obtained by passing the mixed gases through a solution of potassium hydroxide.

In preparing the mixed fluorides on a large scale, fluorine was passed over sulphur in a horizontal copper tube, and the resulting fluorides were passed into a copper spiral which was cooled down to —80°. This spiral dipped into a glass flask through which was circulated a slow current of pure and dry nitrogen. Under these conditions the two fluorides are completely liquefied. The spiral is then warmed very slowly, and the gases obtained are collected in dry glass flasks. That portion of the gas which comes off first is neglected because it always contains some nitrogen. By repeat-

[1] Compt. rend., 130, 865-871.

ing this process of liquefaction and vaporization all the nitrogen can be removed. The mixture of gases thus obtained is exposed to a concentrated solution of potassium hydroxide for several hours. The remaining gas is dried with fused potassium hydroxide. In order to purify this final product completely, it is cooled down to —80° and allowed to solidify. Then, when it is again converted into a gas, the first portions of gas obtained are neglected because they might contain traces of nitrogen.

The perfluoride of sulphur, which corresponds to the formula SF_6, is a colorless, inodorous, tasteless, and incombustible gas. It solidifies at about —55° to a white crystalline mass, which liquefies, and boils at a temperature slightly higher than the temperature of solidification. It is only very slightly soluble in water and in absolute alcohol. Although it is so rich in fluorine, it is remarkable that it is one of the most inert substances, and for the most part its properties resemble those of nitrogen rather than those of the chloride of sulphur. It is not acted on by a concentrated solution of potassium hydroxide, nor is it attacked by copper oxide at dull red heat. It is not decomposed by a fusing mixture of potassium hydroxide and lead chromate. Heated in a closed tube to a temperature at which the glass softens, it undergoes no change, the glass remaining unattacked by it.

When subjected to the influence of the electric spark of a Ruhmkorff coil capable of giving a spark 8–10 cm. long in air, the perfluoride of sulphur is partly decomposed. In one experiment there were obtained 23.30 per cent of a gas soluble in water with the deposition of silica ; 44.36 per cent of a gas soluble in potassium hydroxide ; and 33.33 per cent of undecomposed perfluoride. After sparking the perfluoride for two hours and thirty-five minutes, 11.64 per cent of it still remained undecomposed.

Heated with hydrogen, the perfluoride of sulphur suffers no change, but when a mixture of these two gases is sparked, hydrofluoric acid and hydrogen sulphide are formed, and these substances then react on each other in the presence of the glass to form sulphur, hydrofluosilicic acid, and silica.

Fluorine does not react on the perfluoride of sulphur, as is evident from its method of preparation, nor do chlorine nor the vapor of iodine act on it at dull red heat.

Oxygen acts on the perfluoride of sulphur only under the influence of a strong electric spark. The perfluoride is then entirely decomposed. If the spark is not strong, an oxyfluoride of sulphur is formed, which is less rapidly decomposed by water than thionyl fluoride.

Fused sulphur has no effect on this new gas, though it is converted into lower fluorides when heated in a sealed tube with sulphur. These lower fluorides attack glass, yielding sulphur dioxide and silica.

The vapor of selenium decomposes the perfluoride of sulphur with the formation of silicon fluoride and the anhydrides of selenious and sulphurous acids.

Phosphorus, arsenic, boron, silicon, and carbon at low red heat have no effect on the perfluoride of sulphur.

Sodium attacks the perfluoride only at the temperature of its boiling-point. Calcium and magnesium react with it at red heat. Copper and silver have no effect on it at the temperature of fused glass.

Hydrochloric acid gas does not react with the perfluoride of sulphur when heated in a sealed tube to the temperature at which glass softens, nor does ammonia gas in the cold or at high temperatures affect it. Hydrogen sulphide, when heated with it, yields sulphur, hydrofluosilicic and silicic acids according to the following equations:

$$SF_6 + 3H_2S = 6HF + 4S;$$
$$12HF + 3SiO_2 = 3SiF_4 + 6H_2O;$$
$$3SiF_4 + 3H_2O = 2SiF_6H_2 + SiO_2H_2.$$

In a later paper Moissan and Lebeau[1] give an account of their experiments undertaken for the purpose of determining the density and the composition. The results are very satisfactory.

The following summary given by the authors is helpful:

By the action of an excess of fluorine on sulphur a new gas, the perfluoride of sulphur of the formula SF_6, is formed. This gas is one of the heaviest known, its density being 5.03. Its composition establishes the hexavalence of sulphur. As a compound of fluorine it corresponds to sulphuric anhydride, SO_3. It is curious to observe that two such active substances as sulphur and fluorine should combine to form a gas which is not attacked by molten potassium hydroxide nor by sodium at its point of fusion.

This new fluoride of sulphur is totally different from the chlorides of sulphur, and it shows once more that in chemistry it is well to beware of analogies. Fluorine, although it belongs to the family of the halogens, possesses a character of its own, by virtue of which it sometimes forms unexpected combinations. C. E. C.

[1] Compt. rend., **130**, 984–988.

REPORT.

Ammonia a Weak Tribasic Acid.

A series of papers has just appeared by Frenzel,[1] working in Göttingen with Nernst, in which the conclusion has been reached that ammonia is a weak tribasic acid. The conductivity of liquid ammonia was first studied. The values which had been obtained by Goodwin using commercial liquid ammonia dried over lime were 1.392×10^{-4} and 1.688×10^{-4}. Frenzel distilled commercial liquid ammonia and dried the gas over lime, then recondensed the gas and determined the conductivity of the liquid. He found 1.1×10^{-5}, a value about one-twelfth that obtained by Goodwin.

He then prepared pure liquid ammonia from pure ammonium chloride and lime, washed the gas in a strong solution of potassium hydroxide to remove any carbon dioxide, and dried it by passing it over soda-lime and finally over potassium copper oxide. The gas was then liquefied in a vessel surrounded by solid carbon dioxide and ether. The conductivity of the liquid ammonia prepared in this way was found in two determinations to be: 1.33×10^{-7}, and 1.47×10^{-7}, a value very much smaller than that which had been previously obtained.

The author then raises the question, what are the ions into which pure ammonia dissociates in order to give any conductivity whatsoever? There are two possible ways in which a molecule of ammonia might dissociate:

$$\text{I.}\quad N_2H_6 = \overset{+}{N}H_4 + \overset{-}{N}H_2;$$

$$\text{II.}\quad NH_3 = \overset{\equiv}{N} + \overset{+}{H} + \overset{+}{H} + \overset{+}{H}.$$

The first method is only a possibility, but is very improbable from what we know about dissociation in general.

The second method would lead to the, at first sight, astonishing conclusion that ammonia is a weak tribasic acid, since, wherever we have hydrogen ions we have acid properties, and when a molecule yields three hydrogen ions it is a tribasic acid.

These are simply suggestions. Before they can have much value they must be tested experimentally. If ammonia is a weak tribasic acid it would not break down at once into a nitrogen anion and three hydrogen cations, but like all weak acids would dissociate in stages. We should have:

$$(a)\quad NH_3 = \overset{-}{N}H_2 + \overset{+}{H};$$

$$(b)\quad \overset{-}{N}H_2 = \overset{=}{N}H + \overset{+}{H};$$

$$(c)\quad \overset{=}{N}H = \overset{\equiv}{N} + \overset{+}{H}.$$

[1] Ztschr. Elektrochemie, 6, 477, 485, 493.

To test this, Frenzel made use of the polarization method. Every ion present in a solution will manifest itself by an irregularity in the polarization curve. It then only remained to work out the polarization curve of pure liquid ammonia, and see whether there were any irregularities corresponding to the three stages of dissociation represented above. To make the liquid ammonia a better conductor a little potassium nitrate, or ammonium chloride, or some other soluble salt was added to it. Every polarization curve showed these irregularities, which were practically independent of the nature of the salt used. These fell in the regions of 0.48, 0.66, and 0.78 volts, and since it was the anode polarization which was studied, it must have been due to the anions $\overline{NH}_2$, $\overline{\overline{NH}}$, and $\overline{\overline{\overline{N}}}$. That these irregularities in the curves are due to the ammonia and not to the dissolved salt is made extremely probable by the fact that they always appeared, whatever the nature of the salt added to the ammonia.

The conclusion that ammonia is a weak tribasic acid is thus, apparently, substantiated by the experiments of Frenzel. He also succeeded in showing that hydrogen separates directly upon the cathode, but this line of evidence is not as strong as that first considered.

This conclusion naturally grates upon our preconceived ideas regarding ammonia, but the author points out that there are a number of well-known compounds of the metals with ammonia which would show that ammonia can act as an acid. Thus:

NH_2Na, NH_2K, $(NH_2)_2Zn$,
NK_2, N_2Mg_3, N_2Hg_3, NAg_3, N_2Al_2, etc.

and this list might be considerably extended.

Here we have ammonia playing the rôle of an acid, forming well-characterized substances with the strongly metallic elements.

Whatever may be our opinion in reference to the conclusions which should be drawn from this work, it is quite clear that our older definitions of acids and bases must give place to new and more comprehensive ones. We seem forced to the physical-chemical definitions of acids and bases. An acid is a substance which yields hydrogen ions under any conditions. Wherever we have hydrogen ions we have acid properties, and, conversely, wherever we have acid properties we have hydrogen ions. Similarly, hydroxyl is the characteristic ion of bases. A substance may be an acid, yielding hydrogen ions under one set of conditions, and a base, yielding hydroxyl

ions under different conditions. This seems to be the case with ammonia. H. C. J.

REVIEWS.

LEXIKON DER KOHLENSTOFF-VERBINDUNGEN. By M. M. RICHTER. Second edition. Hamburg and Leipzig: Leopold Voss. 1899.

The second edition of this valuable work, the first edition of which appeared in 1883, will be welcomed by those who have had occasion to consult the early edition, which has been left far behind in the forward march of the science. Some idea of the great activity in chemistry in the last twenty years can be obtained from a consideration of the material contained in these two editions. In the edition of 1883 about 16,000 substances were classified, while the present edition contains about 67,000, the third edition of "Beilstein" containing about 57,000. The system of arrangement is the same as in the former edition, but a new feature, the percentage composition of about 20,000 formulæ, has been added. The value of this system of identifying chemical substances and the thorough manner in which the system has been worked out has been recognized by the editors of a number of the most important chemical journals, and this feature has been incorporated in their indexes. A copy of this work should be accessible to every chemist. J. E. G.

JAHRESBERICHT ÜBER DIE FORTSCHRITTE DER CHEMIE UND VERWANDTER THEILE ANDERER WISSENSCHAFTEN. Begründet von J. LIEBIG und H. KOPP. Unter Mitwirkung namhafter Fachgenossen herausgegeben von G. BODLÄNDER. Für 1893. Erstes Heft. Braunschweig: Vieweg. 1900. 10 Marks.

The old "Jahresberic ." has had a hard time of it for a good many years, and it has seemed as though it would never be up to date. Recently, Dr. von Buchka has given up the editorship and Professor Bodländer has taken up the work. The publishers now promise the volumes for 1893, 1896, and 1897 in the course of the year 1900, and they express the hope that in a short time the other missing volumes will be finished. This is certainly much to be desired, for, although we have the "Centralblatt" and the "Jahrbuch der Chemie," we still need a carefully edited Jahresbericht, such as the old Liebig and Kopp has generally been.

The first number (Heft), which has just come to hand, numbers 320 pages and deals with general and physical chemistry. The work appears to have been carefully done and to be worthy of the "Jahresbericht." I. R.